EFFECT OF MICRO AND NANO CARBON ADSORBENTS DOPED WITH METAL NANOPARTICLES ON THE REMOVAL OF HEAVY METALS FROM WATER

BY

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IN THE NAME OF ALLAH, THE MOST BENEFICIENT THE MOST MERCIFUL

Dedicated to my beloved mother and father and all teachers who have been there for my guidance ever since I started my education.

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All praise be to ***Allah Almighty***, the most beneficent and merciful. Without His consent this task would never have been possible. May his blessings always shower on us. Love and acknowledgment for my ***dear parents*** whose encouragement, words of kindness and prayers always compelled and motivated me towards the completion of this work. Deep respect, regards and prior acknowledgement for my respected supervisor ***Dr. Nadhir A. Al-Baghli,*** my co-supervisor ***Dr. Basim Ahmed Abussaud*** and my committee members ***Dr. Muataz Ali Atieh, Dr. Abdulhadi A Al-Juhani and Dr. Shaikh Abdur Razzaq***. It was their knowledge, way of teaching, encouragement and motivation which always inspired me, helped me and led me to a successful learning activity and the completion of this thesis work. I am grateful to ***King Fahd University of Petroleum and Minerals*** and the ***Chemical Engineering Department*** for providing me the platform, opportunities and facilities for my research.

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LIST OF ABBREVIATIONS

CNTs	**:**	Carbon nano tubes
MWCNTs	**:**	Multi walled carbon nano tubes
SWCNTs	**:**	Single walled carbon nano tubes
HRTEM	**:**	High resolution transmission electron microscopy
CVD	**:**	Chemical vapour deposition
AC	**:**	Activated carbon
WHO	**:**	World health organization
TGA	**:**	Thermogravimetric analysis
EDX	**:**	Energy dispersive x-ray spectroscopy
ICP-MS	**:**	Inductively coupled plasma – mass spectrometry
SEM	**:**	Scanning electron microscopy
EDS	**:**	Energy dispersive x-ray spectroscopy

ABSTRACT (ENGLISH)

Full Name : Muhammad Imran Qureshi

Thesis Title : Effect of Micro and Nano Carbon Adsorbents Doped with Metal Nanoparticles on the Removal of Heavy Metals from Water

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Carbon nano tubes (CNTs) and activated carbon (AC) impregnated with iron oxide, aluminum oxide and silver nano particles were synthesized and used to adsorb chromium (Cr(VI)), arsenic (As) and lead (Pb) from water. The materials were characterized using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), Braunner Emmett Teller (BET) and thermos-gravimetric analysis (TGA). The results of characterization show a remarkable increase in the surface area of the synthesized materials.

The effects of pH, agitation speed, adsorption time, adsorbent dosage and initial concentration of metals in water on the removal efficiency were studied. The adsorption time and pH were found to affect the removal efficiency to a great extent as compared to all other parameters. At pH 6, maximum removal was achieved on the surface of all synthesized materials for different experimental runs.

The first and pseudo second order models were used to fit the kinetics adsorption data. The results show that the pseudo 2^{nd} order kinetics model was the best. The data shows that the rate constants are in the range of 0.19 to 0.763 $mg.g^{-1}.min^{-1}$ and the equilibrium adsorption capacity is in the range from 0.1 $mg.g^{-1}$ to 0.5 $mg.g^{-1}$.

Fruendlich and Langmuir models were used to fit adsorbed phase/bulk phase equilibrium data. The results show that the Langmuir model better fits the data. Values of equilibrium constants extracted from the data range from 0.19 to 1.5 $L.mg^{-1}$ while the equilibrium adsorption capacity ranged from 0.1 to 1.3 $mg.g^{-1}$.

خلاصة الرسالة

الاسم الكامل: محمد عمران قرشي

عنوان الرسالة: تأثير المايكرو نانو والممتصات الكربونية المخدرة مع النانوية المعدنية على إزالة ال معادن الثقيلة من المياه

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: مايو 2015

تم تطعيم مازات أنابيب الكربون المتناهية الصغر ومازات الكربون المنشط بعدة أكاسيد وهي أكسيد الحديد وأكسيد الألمنيوم بالإضافة إلى الفضة من أجل استخدامها في امتزاز بعض الجزيئات المعدنيه من المياه الملوثة وهي الكرومات والزرنيخ والرصاص. تم معاينة جميع المازات قبل استخدمها بعدة أجهزة وهي جهاز الماسح الضوئي وجهاز التحليل الطيفي للأشعة السينية وجهاز قياس المساحة السطحية للجزيئات بالإضافة إلى التحليل الوزني الحراري. أظهرت النتائج زيادة ملحوظة في المساحة السطحية للمازات الجديدة.

تم دراسة تأثير عدة عوامل على فعالية إزالة هذه الجزيئات المعدنيه من المياه مثل درجة الحموضة وسرعة التهيج وزمن الامتصاص والكمية الأوليه من المازات والتركيز البدائي لهذه المعادن في المياه. كان لدرجة الحموضة التأثير الأكبر على فعالية الإزالة مقارنة مع العوامل الأخرى. وأظهرت النتائج أن أفضل فعالية لإزالة المعادة كانت على درجة حموضة 6 لجميع المازات المطعمة.

تم نمذجة معلومات الإمتزاز الحركي باستخدام نموذج الحركة الأولي ونموذج الحركة شبه الثاني. تبين من معلومات المقارنة أن نموذج الحركة شبه الثاني كان أكثر دقه في تفسير معلومات الإمتزاز الحركي. كما أظهرت النتائج أن ثوابت سرعة التفاعل كانت في حدود 0.19 – 0.763 ملغم/(غم.دقيقة) وأن سعة التوازن للامتصاص كانت في حدود 0.1 – 0.5 ملغم/غم.

تم استخدام نماذج لانغميور و فريندليخ لنمذجة بيانات التوازن الإمتزازي. وأظهرت النتائج أن نموذج لانغميور كان أكثر تناسبا مع النتائج. وأعطى قيم ثوابت توازنية تتراوح بين 0.19 – 1.5 لتر/ملغم بينما سعة الامتصاص عند التوازن كانت تتراوح ما بين 0.1 – 1.3 ملغم/غم

CHAPTER 1

INTRODUCTION

1.1. General Introduction

Nanotechnology has opened new avenues of research and development in different fields including those of engineering. It involves the formation of such materials or structures which range in size from 1 to 100 nanometers. Development and study of new materials is more than attractive for people related to various fields of study. Modification of already available nanomaterials is also an exciting aspect. Finding and using new precursors is helpful in imparting new and unique properties to nanomaterials. Advances in nanotechnology have been seen at a rapid rate with growing study and development of different nanoparticles and powders, coating particles, their use in electrical and optical devices and in various fields of materials and mechanical engineering as well.

Undoubtedly, the influence of nanotechnology cannot be eliminated in the coming years from the field of science and technology.The vastness of the field of nanotechnology cannot be denied and because of this vastness we observe the science of nanomaterials moving in different directions. One direction in which it is headed is the one towards carbon structured nanomaterials. One good example in this case is of the carbon nanotubes.

Carbon based nanomaterials are getting special attention. One reason behind their growing importance is the fact that they are commercially rich products. The discovery of carbon nanotubes, carbon nano fibres and buckminister fullerene has brought about great innovation and ultimate attraction towards these nano structures[1].

Apart from the electrical, mechanical and optical properties of these materials, the chemical properties are of extreme value as well. For example, the adsorption capability of carbon materials has long been regarded as a benefit for various chemical reaction applications. Carbon nanotubes belong to this class of nanomaterials and possess great potential in terms of different applications including electrical, optical, water treatment, etc. they were discovered in 1991 and since then they have been found to be chemically highly sTable with great surface area and excellent electrical and mechanical properties [2].

The use of carbon nanotubes to treat water is growing day by day with development of different modification technologies in these materials. They are found to be good adsorbents for different organic and inorganic contaminants found in water. For example, heavy metals become a part of ground water once they are expelled from chemical industries such as the process industries and leather tanneries [3]. These are harmful for human health and need to be eradicated.

1.2. Water Treatment

The treatment of water has become quite essential in the era in which we are spending our lives at this time. There are detailed and specific reasons for this particular statement. It is a very obvious fact that due to increase in human activities specially regarding the advancement in technology, the mankind is on a verge to be badly affected by pollutants in one way or the other. Water being a very important component of life needs to be consumed in a very pure form or otherwise it will be harmful for human health. Various activities including industrial, agricultural, municipal, etc, render water as polluted by addition of various materials that need not to be present in it specially the drinking water which has to become part of the human body in some way. The problem is that we cannot

really imagine our lives with the benefits of the above mentioned sectors as well and this is where we come across a very common phrase that to achieve something you might have to lose another. But here it must be noted that technology advancement and research activities have solved this problem to a great extent and its betterment still continues. Different water treatment techniques are present together with very versatile equipment in order to purify and get rid of contaminants in water.

Another important factor is the realization of different contaminants in water. This particular work is considered with the heavy metals that are present in water and can be fatal for humans if inhaled to a certain extent. This marks the importance of such a procedure which should be used to remove these heavy metals from water. A further step in this regard would be make that procedure more efficient so that the maximum benefit of treatment can be attained. The heavy metals that are under research include arsenic (As), lead (Pb) and chromium (Cr (VI)).

In order to remove these metals from water a proper procedure needs to be defined. Moreover, the materials that are going to be used for this purpose also have a marked importance. The research underway includes the use of nanomaterials for this purpose and those too not alone but with a certain level of impregnation (decoration) of other materials. The materials that are going to be used include carbon nanotubes (CNTs) and activated carbon (AC). These are the basic materials that are going to be in major quantity. Apart from these, impregnation of other materials onto the surface of these three will be considered. These materials are going to be impregnated with the oxides and carbides of iron, silver, aluminium and titanium. The flexibility in the research demands the use of different percentages of these being impregnated onto the basic raw materials. For this

study and research we will be using 1% and 10% impregnations of the above mentioned carbides and oxides. Preparation of the final impregnated materials is an integral part of this research.

The procedure adopted to eradicate heavy metals using the impregnated materials is going to be the adsorption technique whereby it would be studied that what quantity of the heavy metals is adsorbed (removed) using the respective prepared materials.

1.3. Significance of Study

There is a number of factors as to why this particular topic is being researched on. It is a well-known fact that heavy metals are very dangerous contaminants of water. They adversely affect the human health causing severe diseases that are often proven to be fatal. Although one may not see the negativity of these contaminants at once, yet chronic exposure can lead to declining health as mentioned above. Research has indicated that it is very important to get rid of these heavy metals in order to conserve human health. For this purpose, treatment of water is necessary. With the passage of time more and more new and different techniques of water treatment are being introduced together with a different set of materials or chemicals being used to treat them. This research has one of its motivation as in to improve the quality of water.

It has been seen over years that carbon materials have been very good adsorbing agents. This fact will be utilized in this research for the adsorption of heavy metals onto the surface of different carbon materials. The excellent properties of the three important carbon materials including carbon nanotubes, activated carbon and graphene oxide will be considered in this regard. Moreover, to give this research a new and different approach, the

surface of these materials will be impregnated with oxides and carbides of some metals. The results for this new approach are also a motivation towards conducting this research.

As will be discussed in the literature review that there has already been quite a lot of work started on nanomaterials and their different uses and applications in various sectors, even then, the gaps that have been left unfilled in this research regarding chemical engineering and the successful trial of new substances is still a challenge which has been undertaken in this particular case. Just to quote as a simple example, it must be noted here that the removal of Cr (VI) metal is a new in many perspectives as will be discussed in the section of literature review.

1.4. Objectives of the Study

Considering a broader perspective, the following objectives will be achieved in this work:

1- Surface impregnation of CNTs, activated carbon and graphene with metal oxide nanoparticles using metals such as Fe, Al and Ag.
2- Surface impregnation of CNTs, activated carbon and graphene with metal carbide nanoparticles using metals such as Fe, Al and Ag.
3- Characterization of the surfaces of raw and impregnated CNTs, activated carbon and graphene with metal oxide and metal carbide nanoparticles using TGA, Zeta Potential, FE-SEM, XRD, EDX and TEM.
4- Removal of Cr (VI), Pb and As from water using both, raw and impregnated CNTs, activated carbon and graphene.
5- Optimization of the removal parameters such as agitation speed, contact time, pH, dosage of carbon adsorbents and loading of metal nanoparticles.

6- Study of the kinetics of adsorption.

The preparation of materials was done by impregnating or decorating the materials with the respective metals' oxides and carbides mentioned. Two different mass percentages of the nanoparticles were impregnated onto the surface of carbon materials.

The characterization of the prepared materials was brought about using some specific equipment and tests used for determining various physical properties of materials. The verification of the preparation process was also achieved by the results of characterization. Characterization techniques of TGA, SEM and EDX were employed whose results are mentioned in the following chapters.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Nanotubes

2.1.1. History of Carbon Nanotubes

As the name suggests, carbon nanotubes are nano structures which intern are lengthy tubes or cylinders made of very thin layers of graphite. These are open from one end and closed from the other forming a hemisphere of a bucky ball. Fullerene, a carbon allotrope is the basic family of these materials. They were discovered in the year 1991 by Sumio Ijima[2]. Their preparation was brought about using the arc discharge method. Later, they were characterized using transmission electron microscope with a high resolution (HRTEM) [2]. It's now more than two decades that carbon nanotubes were discovered and since then they found huge attraction in various applications and have helped scientists in finding new avenues of research as well. This attraction towards carbon nanotubes is highly attributed to its extra ordinary mechanical, electrical and chemical properties.

2.1.2 Types of Crabon Nanotubes

Basically, carbon nanotubes are categorized assingle-walled (SWCNTs) carbon nanotubes and multi-walled carbon nanotubes (MWCNTs). Typically, SWCNTs possess a diameter which is close to 1 nm but as far as their lengths are concerned, the carbon nanotubes can be thousands of times longer than their diameters. A one atom thick sheet of graphite is known as graphene and it is this sheet which is rolled into a cylindrical form to bring into shape the carbon nanotube. The orientation of graphene sheet wrapped in the form a tube

is represented by the chiral vector containing a pair of indices with integers n and m. these integers represent the number of unit vectors along two directions in the crystalline structure of carbon nanotubes. The nanotubes are said to be “zigzag” if m=0 and if both integers equalize, “armchair” nanotubes are obtained. Other than these, the carbon nanotubes will be the “chiral type” as shown in Figure. 2.1.

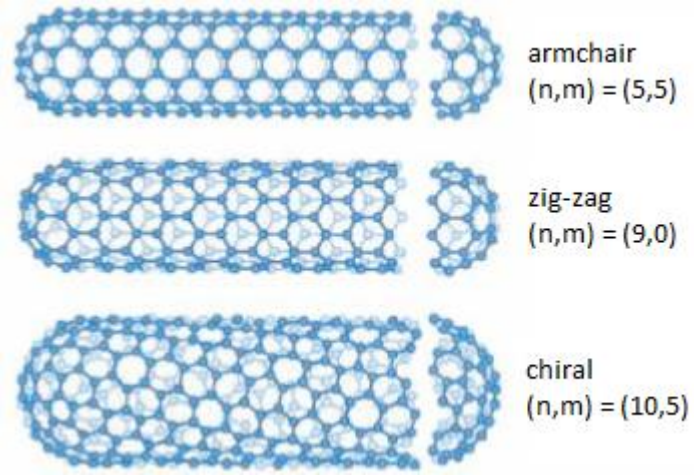

Figure 2.1 Types of carbon nanotubes structures [4]

The other type of carbon nanotubes, the multi-walled carbon nanotubes (MWCNTs) are a combination of concentric SWCNTs and they possess different properties than SWCNTs and also different values of length and diameter. MWCNTs were created for the first time in the year 1992 by Ebbesen and Ajayan. Figure. 2 gives a picture of the MWCNTs.

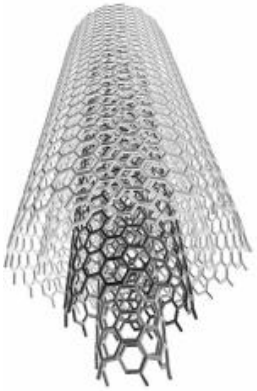

Figure 2.2 Scemetic theoretical model for MWCNTs

2.1.3 Properties of Carbon Nanotubes

2.1.3.1 Mechanical Properties

Carbon nanotubesare very strong materials when it comes to the tensile strength and elastic modulus. This strength is imparted because of the covalent sp2 bonding of the carbon atoms within the structure of carbon nanotubes. Moreover, carbon nanotubes have the highest value of Young's modulus among all the tubes as given in Table2.1. According to a study, the elastic modulus of carbon nanotubes is found to be larger than 1 TPa which is just 0.2 less than that of diamond and the strength is remarkable with almost 100 times greater than that of steel[5].

Table 2.1 Mechanical properties of carbon nanotubes[6]

Mterial	**Young's Modulus (GPa)**	**Tensile strength (GPa)**	**Density (g/cm3)**
SWCNT	1054	150	
MWCNT	1200	150	2.6
Steel	208	0.4	7.8
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

Structurally, carbon nanotubes are elastic in nature which is why they can be easily bent, twisted, flattened or elongated before getting fractured. The diameter of a carbon nanotube is important as it effects the values of elastic modulus, bulk modulus and Poisson's ratio. For example, for a tube with diameter 1.2 nm, the bulk modulus was found to be about 38 GPa [7].

2.1.3.2 Thermal Properties

Similar to the excellence of mechanical properties of carbon nanotubes is extra ordinary nature of their thermal properties. Phonons have been used to find the values of thermal conductivity and specific heat of carbon nanotubes. MWCNTs prepared in CVD were subjected to measurement of thermal conductivity between a temperature range of 4 to 300 K but the vakues varied and did not show a maximum due to the Umklapp scattering effect [8]. Anyhow, carbon nanotubes are highly thermally conductive. In another study, a similar behavior of the carbon nanotubes was observed but only this time the tubes were in the form of a bundle of SWCNTs and the temperature ranged from 8 to 350 K[9]. Similar results can be seen for MWCNTs in the range of 10 to 300 K and bundles of SWCNTs (d=1.3 nm) in the range of temperature of 1 to 200 K [8].

2.1.3.3 Electrical Properties

Carbon nanotubes possess exceptional electrical properties as well. According to a study, they have the ability to carry electric current with a capacity 1000 times more than the traditional copper wires used for electricity [10]. The electrical nature of carbon nanotubes depends highly on its type. The values of the integers n and m are very important in this regard. All armchair nanotubes are metallic in nature whereas others, where n-m is a multiple of 3, the carbon nanotubes behave as a semiconductor.

2.1.3.4 Chemical Reactivity

The chemical reactivity of carbon nanotubes is dependent on the pi-orbital mismatch for which increase in curvature is a big reason. So, the end caps and side walls of a tube have significance here. This is the reason why a carbon nanotube with a smaller diameter is

better in chemical reactivity. However, a change in the covalent nature of either the side walls or the end caps is equally possible [11].

2.1.3.5 Optical Activity

Physical properties of carbon nanotubes such as optical activity fade out as the size of carbon nanotubes becomes larger which has been seen in the case of chiral type nanotubes [5]. Various optical devices, where carbon nanotubes are applicable, can be made better by making use of this optical nature.

2.1.3.6 One-Dimensional Transport

Quantum effects take place in carbon nanotubes because of their dimensions at nano scale. This results in the electron transfer and they ultimately propagate along the axis of the tube only. It is this very characteristic of the carbon nanotubes due to which they have been termed as one dimensional structures.

2.1.4. Applications

Carbon nanotubes have not only opened new avenues of research rather they have already been tried and are continuously being used in various applications. Their immensely unique thermal, electrical, mechanical, optical and chemical properties have marked a great significance in various fields of life including chemical industries. Some applications of carbon nanotubes are listed as below:

1- Chemical sensors

2- Field emission materials [12]

3- Catalyst support [13]

4- Various electronic devices [14]

5- Highly sensitive nano balances for nanoscopic particles [14]

6- Reinforced composite materials [15]

7- Nano probes in the field of meteorology, chemical and biomedical researches [15]

8- As an anode in Li-ion batteries [15]

9- Supercapacitors [16]

Apart from these applications and uses of carbon nanotubes, they have also found prominent applicability in the field of water treatment as means of removing various contaminants from water [17].

According to one of the studies, carbon nanotubes can be converted into diamond when treated under high temperature and high pressure in the presence of a specific catalyst [18].

2.2. Activated Carbon

2.2.1. Introducing Activated Carbon

We often come across effluents which contain pollutants that are in dissolved form. These might be organic or inorganic. It is essential to remove them. For this purpose, one method that can serve well is the process of adsorption. Adsorption uses various materials as adsorbents which have the ability to adsorb substances onto their surfaces, mainly on the pore walls. Different types of adsorbent are in use including activated carbon, silica gel, molecular sieves, alumina, etc which play an important part in adsorbing pollutants from water, soil and air [19].

Activated carbon among these, is considered to be highly efficient as it possesses the ability to effectively remove pollutants and contaminants from water as in the applications of water and waste water treatments. Specifically, activated carbon is used to remove toxic

materials such as phenols, insecticides and herbicides, heavy metal ions and other organic, inorganic and biological materials from water [19].

Activated carbon (AC) is a highly porous solid with a large surface area (500 – 2000 m^2/g). Moreover, its surface reactivity is very high. Micropores are fine pores on AC that enhance the inner surface area as well. These properties of AC allow the physical adsorption of various materials including gases, liquids and solids [19].

2.2.2. Applications

High adsorption capability of AC, makes it highly applicable in domestic as well as industrial sectors. Its big use in industry is related to the removal of gases in filtration systems. In automobiles, AC is used to control the emission of fuel vapors like those of gasoline. Cigarettes use special modified grades of AC to absorb harmful substances in tobacco while smoking. Heavy metals are present in water which have proven to be highly dangerous for human health. AC is used as an adsorbent to remove these ions from water through adsorption. Acidification of the surface of AC helps in the removal of these cations[20-25].

AC is hydrophobic and generally it is more efficient in adsorbing organic molecules from aqueous solutions. Consequently, it can be used for purification of items being produced in various chemical food and pharmaceutical industries. Some other noTable uses and applications of AC are listed as follows [19]:

1. Removal of colour and impurities from sugar to prevent foaming and retardation of crystallization in the process
2. Decolourizing the waste streams from dying industries
3. Removal of valuable substances from gases and liquids in electroplating baths

4. Adsorption of poisonous gases in gas masks
5. Tertiary treatment of waste water using fixed beds of AC
6. Adsorption of contaminants in vegeTable and animal oil

2.2.3. Preparation

Materials containing carbon can be converted into AC by different chemical methods. Normally, the sources of carbon used are wood, charcoal, nut shells, fruit pits, paper mill waste and even PVC. Coconut shells and apricot pits have been found to be the best sources of good quality AC manufactured [26-30].

There are two main processes used to prepare AC. Namely:

1. Physical activation (gas activation)
2. Chemical activation

The choice of either of these methods depends on the source of carbon material being used and also on the end type of AC required which may either be in powdered form or granular one. Moreover, the density (high or low) of the AC prepared also depends on the type of process used. In the physical activation method, carbonization of the raw material takes place at about 400-500°C of temperature followed by oxidation using gases such as carbon dioxide and steam at temperatures ranging between 800 and 1000°C. Pyrolysis starts at about 225°C [26-30].

The products obtained as a result of incomplete combustion are burned because of the very high temperature used in the thermal treatment. Due to the removal of such products as tar, there is an exceptional increase in the surface area of the product. During the preparation of charcoal, some incomplete combustion products cover the open pores of the material which reduce its sorption power. These products are eradicated once activation of charcoal

takes place and ultimately, the activated material formed has open pores giving it a huge enhancement in surface area. Vapour adsorbent carbon materials are formed from nut shells or pits using the physical or gas activation method. They possess a pore diameter less than 3 nm and are hard materials. In this case, carbonization takes place first followed by activation at 800 to 1000°C. On the other hand, chemical methods allow carbonization and activation to take place simultaneously. The organic molecules or hydrocarbons formed during the process are removed when calcination takes place in a furnace. Rotary kilns are used for calcination which heated from the inside.

Activation with zinc chloride at low temperatures of 600 to 700°C gives a high yield of decolorized carbon.

Commercially, activated carbon is sold as a gas adsorbent or a liquid adsorbent. The later is usually in the form of powder or granules having a high area to volume ratio due to which the efficiency of the adsorption process is increased. Regeneration of granule form is quite possible by washing with different chemicals namely acids, organic solvents, etc or simply heating them up under vacuum but it is very difficult to regenerate the powdered form of activated carbon once used.

The pore size of activated carbon decides the size of molecules that can be adsorbed and the surface area depicts the amount of material that can be adsorbed. Moreover, the presence of various other materials including hydrogen, oxygen, etc make acidic and assist in the adsorption process depending on the contaminant to be removed or adsorbed [19].

2.3. Toxicity of Heavy Metals

It has already been mentioned in the objectives of this study that removal of heavy metals will be performed. The heavy metals which have been focused upon in this case include

lead (Pb), arsenic (As) and chromium (Cr). The purpose of selecting these metals as water contaminants is satisfied by a number of reasons of their toxic nature. Toxicity of these heavy metals and its possible effects on human health have been discussed in this topic.

2.3.1. Chromium and Its Toxicity

For the first time, chromium metal was found in the year 1797 by Louis Nicolas Vauquelin. Chromium has been named after a Greek word *hroma* which means colour. It was named such because chromium compounds are very colourful in nature [31]. Chromium is an abundant element found in nature with more than one oxidation states or valancies ranging from +2 to +6. Divalent chromium is not sTable and quickly gets converted to the trivalent form. Chromium is found in water, soil, air and the lithosphere. The most important ore of chromium is known as chromite ($FeCr_2O_4$). Although chromium is found in solil to a great extent, yet its quantity in natural water is quite rare compared to the concentration of natural background amounting to 1 µg/L. greater concentrations will indicate anthropogenic pollution.

Chromium is potentially harmful to human health. It can infect the skin and bring about ulcerations. Damage of the nasal tissue, respiratory problems are created by exposure to chromium which may also lead to lung cancer. Cr (VI) is converted to Cr (III) as it enters the blood circulation system. The human body immune system is greatly affected by Cr (VI) and Cr (III)[3]. The human lymphocyte is killed by intake of either Cr (V) or Cr (VI) leading to apoptosis[32]. According to a detailed study, Table. 2.2listsvarious effects on human health caused by chromium.

Chromium is a metal which is found in the form of ores together with other elements as well. Commonly known ores include ferric chromite ($FeCr_2O_4$), crocoite ($PbCrO_4$), and

chrome ochre (Cr_2O_3). Chromium is considered to be one of the most occurring element inside the earth's crust and it is 6th most abundant transition metal of the world [33]. Moreover, chromium is another toxic metal found in drinking water. According to the WHO, only 0.05mg/L of chromium is accepTable in drinking water [34]. In comparison, Cr(VI) has much more toxicity than Cr(III) [35]. Cr(VI) is often found in water streams near industries and is hazardous for health in regards that it can cause diseases such as pulmonary congestions, vomiting, and severe diarrhea. It can also damage the liver and kideny [36, 37]. Industrial activities like tanning, finishing of metals, electroplating, textile manufacturing and chromate formation make use of chromium [38]. This indicates that the major source of chromium to the environment is the waste water coming from industries which includes the blowdown from cooling towers, electroplating and other coating operations. Cr(VI) is found in different forms which entirely depends on the pH of water. It can be found as dichromate ($Cr_2O_7^{2-}$) ions, chromic acid (H_2CrO_4), chromate ion (CrO_4^{2-}) and hydrogen chromate ion ($HCrO^{4-}$).

Table 2.2 Effects of Cr on the health [32]

Where it can effect	Effect
Eye	Eye irritation and burns
Skin	Skin becomes sensitive and a reaction may start on the skin on next frequent exposure. Skin injury and abrasion
Ingestion	Damaged kidney, gastrointestinal tract irritation causing nausea and vomiting
Inhalation	Damaged liver and kidney, ulcers in the nasal septum, respiratory tract irritation and burns

2.3.2. Arsenic and Its Toxicity

Both, natural resources and human beings are responsible for amounts of arsenic in water sources. Arsenic can move into the ground water due to the geological formations that take place in the sedimentary rocks, the geothermal water and the weathered volcanic rocks. Mining activities, metallurgy, preservation of wood and the use of pesticides also introduce arsenic in water. The allowable limit of arsenic by the WHO is 10 ug/L. 21% of the ground water and 10% of the surface water is contaminated with more than 5 ug/L of arsenic according to a survey by The National Arsenic Occurrence Survey[39]. Arsenic is most likely to be a cancer causing material and it is this fact which has put the world in a fix to think for its efficient removal from water. In Taiwan, India and the West Bengal, excess levels of arsenic have been found in waters which are much more than what is allowed by the WHO. Drinking water contaminated with arsenic causes various diseases that include cancers of skin, lungs, bladder and kidney and various other tumors. Diabetes, vascular diseases and in the extreme cases, weight loss of new born babies and infant mortality have also been reported as a result of arsenic contaminated drinking water. Different researches have been conducted to cut down arsenic levels in water economically. Resultantly, techniques such as ion exchange, lime softening, coagulation, iron- manganese removal using activated alumina and other specific methods like reverse osmosis and ultrafiltration have been employed to serve the purpose.

Arsenic as a contaminant, pollutes water and renders it unsafe for use specially for drinking purposes. It seems to be a problem all over the world with reports coming from several countries including the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India [40, 41]. It must be mentioned here that arsenic

exists in two different oxidation states of +3 and +5. Oxidation state is important with regards to the level of toxicity of an element. For example, the trivalent species of arsenic and antimony are much more toxic than their pentavalent ones [42]. Arsenic is present in environment in combination as different organic and inorganic forms [43]. Some rocks and sediments contain arsenic which are the cause of arsenic leaching into natural water streams [41-44].

Acute poisoning of arsenic may take place as a result of intake of the element through food. It will probably result in burning, unusual pain, vomiting, diarrhea, cramps, and certain abnormalities related to mouth, throat and heart [45]. Compounds containing arsenic which are in the inorganic form hundred times more toxic than those which are organic in nature (DMMA and MMAA). Moreover, the effect of arsenic is much large if it is taken for a long period of time. It can cause various diseases and health effects like the hyperkeratosis, hyperpigmentation, cardiovascular diseases, damage to the nervous system, skin cancer, hepatomegaly, gangrene and splenomegaly. Arsenic taken in high concentrations from drinking water may also result in a severe effect of spontaneous abortion. The presence of arsenic in ground water of Bengal in India is one of the biggest problems in this regard [39].

2.3.3. Lead and Its Toxicity

Lead is a metallic element with the symbol Pb. It's has been originated from the latin word plumbum. Lead belongs to the category of heavy metals and is highly toxic. General applications of lead include constructions, batteries, solders, alloys, etc. Moreover, in order to store corrosive liquids such as sulfuric acid, lead lined containers are used which might

further be treated with other metals such as antimony, to enhance the toughness. Lead is a neurotoxin and it is capable of accumulating in bones and tissues.

The contamination of lead in water or drinking water to be more specific, might be because of a number of reasons. One such reason includes the plumbing faults or wear and tear of lead solder joints in pipes as time passes by. Plenty of chemical industries are responsible for the presence of lead in wastewater streams. These industries include the battery production factories, printing, dying, etc [3]. Lead based paints are normally one major cause of lead in environment. It can be found in various amounts in soil, air, dust and food cans.

As water has to be consumed by the human body, it needs to be free of lead because of the fact that it is potentially toxic to human beings. Lead is said to become a part of the human blood stream. The maximum contaminant level for lead in water as described by the world health organization, is 0.01 mg/L. 20% of the lead consumed by human body from various sources comes from the lead in drinking water. Increase in the amount of lead in an adult human being results in disorders related to blood pressure and hearing. Most importantly, the category of human beings highly effected by lead contamination of water include young children, infants and pregnant women. Apart from the above mentioned health effects of lead, some other important organs of the human body are said to be effected if lead intake is more than 0.01 mg/L. These include the kidneys, brain, heart and blood vessels. Male sperm count is also decreased by lead in human body. Lead can be transferred from the body of mother to her infant through breast feeding and a pregnant women can transfer lead to the fetus from her blood [3].

Lead is found to be hazardous in the environment if it is present in large quantities. If drinking water contains lead and has been used for a long period of time, it will have the ability to cause mental retardation, renal diseases, damage of the nervous system, cancer and irritating disease like aneamia [3]. Lead is a non-biodegradable material and in order to prevent its impacts, it is necessary to remove it from water. Lead is found to be toxic as it accumulates in the body over a period of time. It gets absorbed through the digestive tract and lungs entering into the blood from where it can travel throughout the body. The concentration of lead in this regard is very important. It is the concentration which decides that to what extent it effects the health. If lead is found in any such water source that is used for drinking, it becomes a major source of lead in human body. Infants can take in 40 to 60% of lead through various liquids that they drink made up of water containing lead. Lead even has the ability to produce many chronic and acute diseases in human beings such as irritability, muscle weakness, fatigue, etc.

2.4. Removal of Heavy Metals

In practice, there are many methods employed for the treatment of water with the purpose of removing heavy metals from it. These methods fall in the category of not only membrane technology but also as chemical treatment. We have the examples of reverse osmosis and ultrafiltration as membrane methods whereas other methods used for this purpose include coagulation and flocculation, ion exchanging, lime softening, adsorbtion (using activated carbon, fly ash, peat, metal oxides, etc.). phytoremediation is a biological technology for the purpose of waste water treatment [46, 47]

Some of the methods mentioned above are briefly described as follows:

2.4.1. Reverse Osmosis

Reverse osmosis uses the concept of a semi permeable membrane in order to remove heavy metals from waste waters. The phenomenon behind this method is the pressure created by the dissolved particles in water which is higher in value than the osmotic pressure. Resultantly, the dissolved solids in water are separated from the water content. Reverse osmosis membranes are made up of special polymeric materials which is highly expensive, thus rendering this procedure as an expensive one in water treatment technologies [46]

2.4.2. Electrodialysis

As is evident from the name, the process of electrodialysis makes use of such a membrane which is ion selective. On applying an electric potential, the negative and positive ions move towards their respective electrodes i.e. the anode and cathode respectively. As metal ions in water are positively charged, they are removed by electrodialysis. The electrodes are alternately arranged which creates cells of salts that have different concentrations. During the process metal hydroxides are formed which might result in the clogging of the membrane [46].

2.4.3. Ultrafiltration

Special membrane technology is used which makes use of pressure to get rid of unwanted materials in water including heavy metal ions in waste waters. A lot of sludge is formed as a result [46].

2.4.4. Ion Exchange

Ion exchange resins are used in this process for the purpose of removing positively charged metal ions. The exchange of ions takes place between the resin and the ions present in

water. The electrostatically attached ions in the resin are replaced by the unwanted ions in water. Although this method is quite a conventional one, yet it has certain disadvantages including the inability to remove some specific metal ions and high costs [46].

2.4.5. Chemical Precipitation

Chemicals are used in this kind of treatment which help in removing unwanted materials from water. Coagulants and flocculants make use of adhering to let the particles settle down and form sludge. A large amount of sludge is formed as a result of chemical precipitation which is considered to be a disadvantage of this technique [46].

2.4.6. Phytoremediation

The process of phytoremediation makes use of certain plants which are grown in such a way that they can change the chemical nature of contaminants as the contaminants move up their roots. This method is a decent one to get rid of heavy metals from water but the time taken by these plants for their action is too long [46].

All the methods discussed above are currently in use for the treatment of water including the removal of heavy metals. Although these methods provide a solution for the problem to a certain extent, yet each of them has disadvantages which render them as inefficient in one way or the other. As we have seen, the formation of toxic sludge, high cost and slow speed of process are concerns which need to be addressed in this regard. In order to overcome these problems and satisfy the removal of heavy metals from water in an efficient manner, a new and better technique has to be created.

2.4.7. Adsorption

It hasn't been long that adsorption has been studied and applied in the field of water treatment. It was in the year 2002 when CNTs were found to be useful for the removal of lead from water. It was seen that the adsorption of lead ions on CNTs depended on the pH of the aqueous solution. The CNTs were prepared using nickel as catalyst. The prepared CNTs were refluxed to remove the catalyst particles. The carbon source which was used for this preparation was propylene [36]

A year later, it was the same author who studied the removal of cadmium and copper using the same CNTs and compared the results of the three metals. He found that the adsorption capability of the CNTs used resulted in the removal of these heavy metal ions in the order $Pb^{2+}>Cu^{2+}>Cd^{2+}$[48].

The modification of CNTs by oxidation showed that the adsorption capacity increased for cadmium as functional groups were attached to the CNT surface [48].

Similarly, CNTs were found to adsorb hexavalent chromium from water at pH values from 4 to 7.5.

Both single walled and multi walled carbon nanotubes have been used for the removal of zinc ions from water. It was seen that as the temperature of the solution increases, there is an increase in the adsorption of zinc as well [15].

Using the same type of CNTs, nickel was removed from water through the process of adsorption. Increasing the agitation speed for the solution increased the removal but a decrease was seen with an increase in the CNTs dosage [15].

Activated carbon is another adsorbent that was used to remove different types of metal ions from water namely, manganese, lead, copper, cadmium and zinc. The surface of activated

carbon was also oxidized using different materials including nitric acid, H_2O_2 and ammonium persulfate [49].

2.5. Adsorption Isotherm Models

Adsorption isotherm models are a type of mathematical models which explain the interaction between the species to be adsorbed (adsorbate) and the material that is being used for adsorption (adsorbent). There exist certain factors which play an important part in development of such an interaction like the extent of homogeneity of the adsorbent, the relation between adsorbate molecules and the kind of coverage. According to the Langmuir model, there is no interaction between the adsorbate molecules and mono layer adsorption prevails. On the other hand, the Freundlich model is such a relationship model which describes the adsorption of an adsorbate from the liquid onto the surface of a solid. It assumes that there are different adsorption sites on the solid surface giving a number of adsorption energies. In order to study the adsorption behavior, adsorption isotherms need to be created. Both, Langmuir and Freundlich isotherms are formed for this purpose. The Langmuir isotherm is represented by the following relation:

$$q = \frac{q_m K_L C_e}{(1 + K_L C_e)} \qquad (2.1)$$

Where:

q = adsorption density at equilibrium concentration (of solute) i.e. C_e (mg of adsorbate per g of adsorbent)

C_e = the equilibrium concentration of solute/adsorbate in solution (mg/L)

q_m = the maximum adsorption capacity (mg of adsorbate per g of adsorbent)

K_L = Langmuir constant for adsorption energy

Equation 2.1 can be written in the linear form as:

$$\frac{C_e}{q} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (2.2)$$

The above equation can be used to develop a linear relationship in graphical form by plotting C_e/q against C_e. The Langmuir constants will then be calculated from the slope and intercept of the graph. Although Langmuir is a good option to describe adsorption but if it does not give a good linear fit, other models can be used to serve the purpose.

Freundlich model can also be used to describe the adsorption. It is given by the following equation:

$$q_e = K_F C_e^{1/n} \qquad (2.3)$$

Where:

q_e = adsorption density (mg of adsorbate per g of adsorbent)

C_e = the equilibrium concentration of solute/adsorbate in solution (mg/L)

K_F and n are empirical constants which depend on a number of environmental factors where n>1

Equation 2.3 can be written in the linear form as:

$$Log\ q_e = Log\ K_F + (1/n) Log\ C_e \qquad (2.4)$$

As discussed above, equation 2.4 can also be used to get a linear fitting relationship by plotting log $q_e$vs log C_e. The constants can be evaluated by finding out the slope and intercept of the graph.

2.6. Kinetic Modeling

In order to study the rate at which the adsorbate is uptaken by the solid adsorbent, it is important to perform the kinetic modeling. This rate is related to the residence time of the adsorbate at solid liquid interface. The first and second order rate equations and the pseudo second order rate equations are defined below. These will be used to determine the sorption mechanism of the heavy metals onto the surfaces of CNTs and AC.

2.6.1. Pseudo First Order Model

The first order model is given by the following equation where k_1 is the rate constant of 1st order adsorption.

$$ln\frac{q_e - q_t}{q_e} = -\frac{k_1 t}{2.303} \qquad (2.5)$$

2.6.2. Pseudo Second Order Model

The pseudo second order model is a simple adsorption kinetic model given as follows [50]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2.6)$$

Integrating the above equation implies the following forms where k_2 is the rate constant of pseudo second order adsorption.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (2.7)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2.8)$$

Equation 2.8 will be used to determine the values of q_e and k_2 from the slope and intercept of the graph obtained by this very equation.

Here:

q_e = sorption capacity at equilibrium

q_t = sorption capacity at time t

k_1 = rate constant for the first order sorption

k_2 = rate constant for the second order sorption

2.7. Adsorption Isotherm and Kinetics Modeling – Literature Survey

The kinetics of the adsorption of lead, zinc, nickel and cadmium onto peanut husks carbon (PHC) has been studied using two different approaches. One of them is the first order rate equation and the other being the hyperbolic equation.After conducting experiments at different concentrations of solution keeping the temperature constant each time, isotherm modeling was performed using the Langmuir and Freundlich equations [51].

Modified and non-modified carbon nanotubes have been used to remove trivalent chromium from water and their adsorption kinetics have been studied together with the development of isotherms using Langmuir and Fruendlich equations. The later was found to give a better fit with the value of R^2 being 0.9494 compared to that obtained from the Langmuir model which was 0.9089 [35].

Using three different time intervals, the adsorption mechanism was studied with the pseudo second order rate equation describing the sorption. A comparison of the respective rate constants suggested that modified CNTs used less time to reach equilibrium concentration as compared to raw CNTs [35].

The uptake rate of hexavalent chromium by activated carbon (produced from agricultural wastes) was studied using both, the pseudo first and second order rate equations as well as the intra particle diffusion kinetic models. The chromium adsorption was in fit with the Elovich equation model [52].

The adsorption isotherms for the adsorption of lead and copper onto grafted silica were created using the Langmuir equation which is formed by a combination of the adsorption and desorption rate equations. To study the sorption kinetics, the pseudo first order model, pseudo second order model, Langmuir model and double exponential model were used with the experimental data obtained [50].

Biosorbents were used for the adsorption of heavy metal ions (Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}) from water and the adsorption rates were studied using the pseudo first and second order rate equations. Moreover, both, the Langmuir and Freundlich isotherm models were considered to analyze the equilibrium of experiments. Resultantly, the pseudo second order rate equation was found to best explain the chemisorption taking place as the rate controlling mechanism [53].The Langmuir model was found to be in good agreement with the experimental data with R^2 values reaching upto 0.992 for zinc as compared to 0.968 using the Freundlich model [53].

It was found that for the adsorption of methylene blue onto graphene oxide, the pseudo second order model was in good fit. All R^2 values in this case were seen to be more than

0.99. In order to describe the diffusion mechanism during the adsorption, the intra particle diffusion model was used. Also, the adsorption isotherms were created and the experimental was fitted using both models i.e. the Langmuir and the Freundlich models. The Langmuir model was found to be suitable with R^2 values reaching upto 0.989 [54].

Activated carbon impregnated with silver and copper was used by one of the researches for the adsorption of arsenic from water. Isotherms were obtained using the Langmuir and Freundlich equations. The Langmuir isotherm fits with the experimental data better than the Freundlich isotherm which is good as far as the adsorption reaches in mono layer [55].

Both, Langmuir and Freundlich isotherm models were found to explain the experimental data in a good manner when the adsorption of lead was studied using CNTs functionalized with the carboxylic group. The R^2 values for the isotherms were found to be 0.9731 and 0.9971 respectively. After a close study of the rate equations, the pseudo second order rate equation was found to be the best in explaining the sorption mechanism as the value of R^2 was much smaller for pseudo first order rate equation [56].

CHAPTER 3

METHODOLOGY

3.1. Surface impregnation of carbonaceous materials with metal oxide nano particles

In the experimental section regarding the preparation of materials, three of the carbon based materials were used as basic raw materials, namely, CNTs, activated carbon and graphene. These materials were impregnated by metal oxide and metal carbide nanoparticles in different ratios. The metals whose oxides and carbides were used for this purpose include iron, aluminium and silver. The oxides of these metals were extracted from salts of these metals respectively and were mixed with the basic raw materials each time in ethanol. Two different ratio materials were formed. One of them contained 1% by weight of the metal oxide or carbide and the other contained 10% by weight of the metal oxide or carbide. The mixture in ethanol was subjected to ultrasonic conditions for 30 seconds and the sonicated mixture was kept for drying the ethanol for a period of 12 to 24 hours at a temperature of 60 to 70°C. Sonication is basically used to complete a homogeneous and wetted impregnated product. Similar is the case when the drying procedure is under way. The final procedure involves the most important part which is the calcination of the dried product from the oven. Calcination is performed in a furnace for almost 3 to 4 hrs under a temperature of 350°C. This step finalizes the impregnated product.

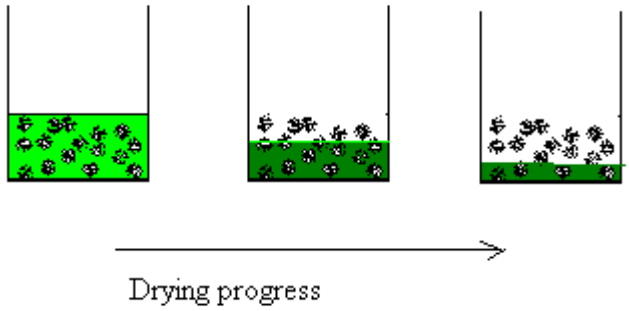

Figure 3.1 The increasing concentration of the metal salt solution during drying.

3.2. Thermal Analysis

Thermal analysis was performed using the TGA (Thermogravimetric analysis). TGA has the ability to record a measure of the loss in weight of a sample as the temperature progresses. It can tell us about the presence of any volatile materials in our sample or even the moisture content. The TGA analyzer is a simultaneous measuring instrument which has the ability to measure the change in mass of the sample together with any change in the phase of the material as well. The TGA analyzer which was used for this particular work has the following features:

1. Material of the furnace is PtRh
2. Temperature range is 25°C to 1500°C
3. Vacuum atmosphere for precise control of measurements
4. DSC measurements show the phase transitions and any decompositions taking place
5. N_2 for inert environment at a pressure of maximum 20 psi
6. Air for oxidation at just less than 14 psi

3.3. Surface Characterization of the carbon materials

For the characterization of the impregnated materials formed, specific techniques and equipment were used. The surface was characterized using scanning electron microscopy (SEM) and EDX. TGA was used for the purpose of thermal analysis as has already been mentioned.

3.4. Standard Water/Metal ions Solutions' Preparation for Treatment

The study is concerned with the removal of heavy metals namely lead, arsenic and hexavalent chromium. 1ppm (1mg/L) solution of each of these metal ions was prepared in water. The glass apparatus used for this purpose was thoroughly washed with 5% of nitric acid so as to prevent any adsorption of the metal ions on the glass surface.

The final volume required for the batch treatment process for each metal was 1 litre of the solution. It was prepared from a standard solution stock of 1000ppm of each of the metal ion. The respective calculations for this purpose are given below:

$$c_1 v_1 = c_2 v_2$$

Where:

c_1 = concentration of the standard solution

c_2 = required concentration of the stock solution

v_1 = volume of the standard solution

v_2 = final volume of the stock solution

3.5. Batch Mode Adsorption Experiments

The experimental portion of water treatment was conducted using 100 ml glass flasks in which about 50ml of water at a specific adjusted pH was spiked with each of the metal ion

solutions one by one. The solution was then subjected to the addition of the prepared impregnated materials. In order to carry out the adsorption experiments, the flasks were put onto a shaker which was shaken at specific speeds each time so that the contaminants are well in contact with the adsorbents and the adsorption takes place.

The pH of the solution was adjusted using 1M solutions of nitric acid and sodium hydroxide. It is important to know the loading of the materials used as adsorbents to find out the weight that gives the maximum adsorption.

Inductively coupled plasma mass spectroscopy (ICP-MS) technique was used before and after the batch experiment in order to determine the removal of metal ions from the water samples. The ICP-MS determines the concentration of heavy metal ions which helps in determining the removal percentage as a result of adsorption. After this, various other parameters such as the dosage of materials, the pH, the contact or residence time, the agitation speed and the initial concentration were studied.

3.5.1. Layout of the Adsorption Experiments

A number of factors were studied which effected the adsorption of metal ions onto the surface of adsorbents. These factors include:

1- The aqueous solution pH
2- The dosage of adsorbent
3- Residence time (time for agitation)
4- Agitation speed
5- Concentration of metal ions in solution

3.5.1.1 Effect of pH

pH of the aqueous solution was varied from 3 to 8 using 1 M solutions of sodium hydroxide and nitric acid. The selected pH range is in accordance with pH values of wastewater obtained from industries like leather tanneries, metal finishing industries and chromate manufacturing industries. Moreover, the pH range for drinking water according to WHO lies in between 6 to 8[34]. The effect of pH was observed on the adsorption capacity of the adsorbents. In order to maintain a constant pH in case of lead ions, buffer solution was used to prepare the stock.

3.5.1.2 Effect of Adsorbents' Dosage

A fixed volume of aqueous solution of each heavy metal element was subjected to different dosages of the carbon adsorbents from 50 mg to 200 mg. This was helpful in determining the adsorption capacity at different range of adsorbents. Because, CNTs are considered to be highly expensive, the maximum dosage value was kept at 200 mg in order to keep the economic feasibility on practical grounds. It is also evident from literature review that this particular range of dosage has been found useful for entire removal of heavy metal contaminants [56]. The removal percentage of metal ions was studied on each dosage and the dosage corresponding the maximum removal of metal ions was selected. Dosage was the second parameter to be selected after pH. 1 ppm of initial concentration of the solution was used.

3.5.1.3 Effect of Contact/Residence Time

The extent of removal of metal ions through adsorption was studied at different time intervals for the contact of adsorbent with the contaminant metal ions in the solution. A fixed agitation speed was employed using time periods of 30 min, 60 min and 120 min.

additional time periods of 240 min and 300 min was used to get the equilibrium in case of certain adsorbents.

3.5.1.4 Effect of Agitation Speed

Agitation speeds of 50, 100 and 200 rpm were used. A random selection was made to determine adsorption capacities at different values. This was the fourth parameter whose effect was studied keeping all other parameters at fixed values corresponding to the maximum removal or adsorption of metal ions. The lab shaker used for this purpose was provided with speed controller which was adjusted as required.

All of the above mentioned parameters were varied one by one in the same order as presented here. For all these parameters, the initial metal ions concentration of the aqueous solution was kept constant at 1 ppm. After each experiment, the contents of the flask were filtered using a 4 category of whatman filter papers and the filtrate was analyzed using the ICP-MS.

3.6. Experimental Design

A systematic data was designed according to matrix model for the heavy metal contaminants as shown in Table 3.1.

Table 3.1 Values of parameters varied in batch experiments

S.No.	Parameters Varied	Values
1	pH of initial aqueous solution	3
		5
		6

		8
2	Dosage of adsorbents	50 mg
		100 mg
		200 mg
3	Time of agitation (contact time)	30 min
		60 min
		120 min
		240 min
		300 min
4	Speed of agitation	50 rpm
		100 rpm
		200 rpm
5	Initial concentration of aqueous solution	1 ppm
		3 ppm
		5 ppm
		7 ppm

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Carbon Nanotubes (CNTs)

The characterization of the CNTs was performed after their impregnation with metal oxides and metal carbides. These characterization tests included the surface and thermal characterization together with the elemental analysis of the modified adsorbents. The techniques used for this purpose include:

1. Thermo gravimetric analysis (TGA)
2. Energy-dispersive X-ray spectroscopy (EDS)
3. Scanning electron microscopy (SEM)

The results of characterization suggested that the surface of CNTs were successfully modified by metal oxide and metal carbide nano particles of the metals, iron, silver and aluminium. The details of these results are represented in the following paragraphs.

4.1.1. Thermo gravimetric analysis (TGA) of CNTs

TGA was conducted at a temperature of 900°C in the presence of air. Air was chosen so as to burn the carbon material present inside the TGA pan. A temperature of 900°C ensures the burning of CNTs with the impregnated metal compound retained in the pan. As the decomposition temperature of metal oxides and metal carbides is greater than 900°C, at the end of the test, it is the only material retained.

The TGA of all the impregnated samples of CNTs showed the presence of some level of impurity in them. This presence of impurity is backed by the retention of some material in

the TGA pan. A certain weight percentage is visible even after the end of the experiment at temperatures nearing to or equal to 900°C. For example, in Figure 4.1, around 30% of the weight of sample is retained in the pan at 900°C. This is because this particular sample of CNTs was impregnated with 10% of iron oxide. Apart from the impregnated material left over, there is also a certain amount of the catalyst (used in the CNT manufacture) left over due to which the retention percentage is high.Moreover, the plots indicate declining points. The major portion of the curve is the one representing the burning of CNTs which can be seen around the 450 to 500°C mark. It has been reported that the burning temperature range of CNTs is 500 to 700°C [57]. If we observe the Figure 4.1, it is visible that the last declining point representing the decomposition of CNTs is different for all the three types of CNTs. For the pure CNTs, the temperature is much higher than those for 1% and 10% impregnated samples. The reason is the levels of impurities (metal oxides or metal carbides) in the CNT samples. Similar is the case with the metal carbide impregnated CNTs. Although the temperature for CNTs has gone further compared to the metal oxide impregnated CNTs, yet the difference among the 1% and 10% impregnated samples follows the same trend.A comparison has also been developed between the different types of impregnated CNTs. If we have close look at the TGA for 10% iron oxide impregnated CNTs and compare it with the TGA for 10% iron carbide impregnated CNTs, a difference in temperature of decomposition of CNTs is seen. The former depicts a temperature of around 500°C and the latter denotes the temperature of around 550°C. This difference is due to the presence of a greater amount of carbon in the form of carbide in the second material.

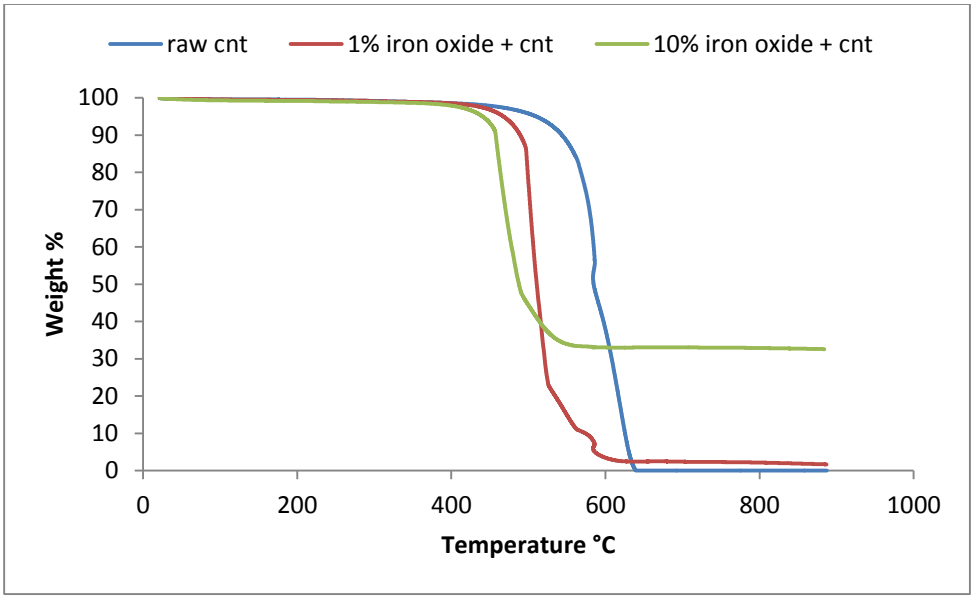

Figure 4.1 TGA comparison (pure CNTs and iron impregnated CNTs)

4.1.2. Energy-dispersive X-ray spectroscopy (EDS) of CNTs

EDSis and elemental analysis which indicates the percentage of each element present in the sample material. EDS was conducted by preparing a small amount of the sample each time on a round metal element to be placed in the SEM chamber for testing. The sample was coated with platinum metal. The results for the EDS of CNTs are shown in Figures 4.2 to 4.5. In each of the presented graphs, there are present peaks, each of which represents an element. The exact percentage of each element in the sample is also tabulated in Table 4.

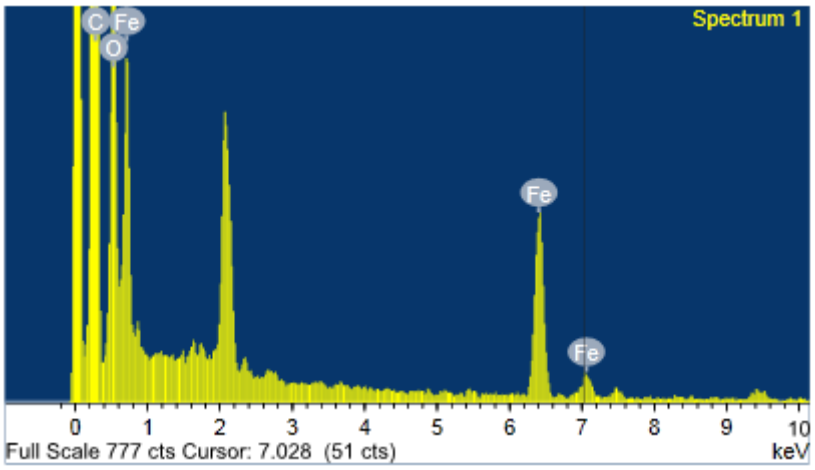

Figure 4.2 EDS for iron oxide impregnated CNTs

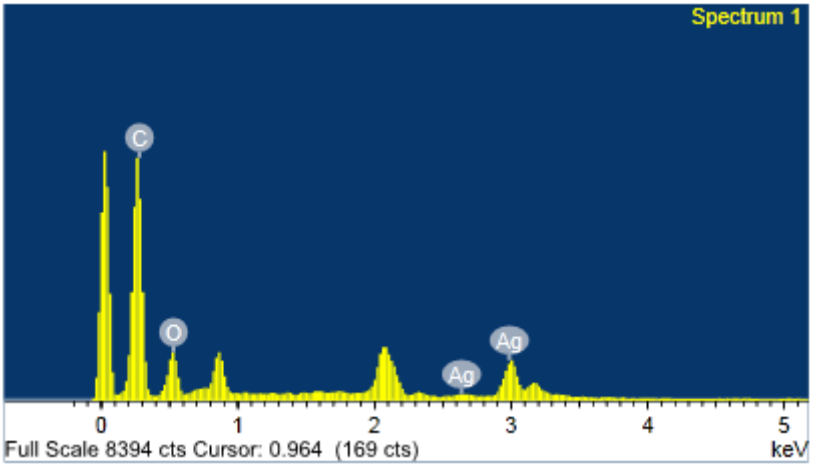

Figure 4.3 EDS for silver impregnated CNTs

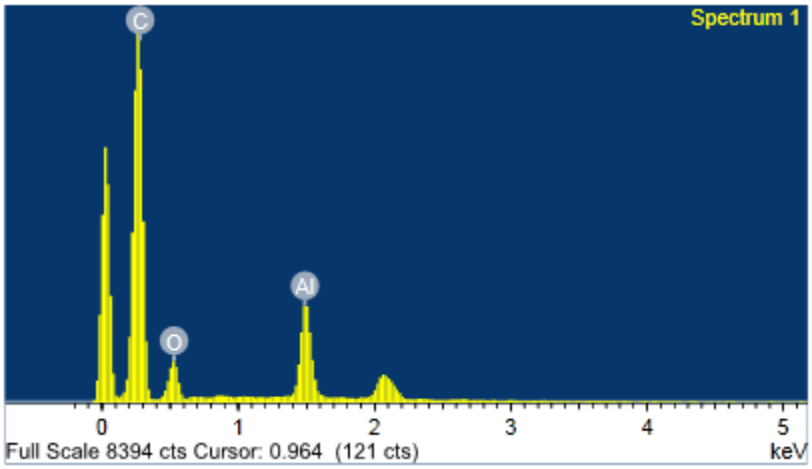

Figure 4.4 EDS for aluminium oxide impregnated CNTs

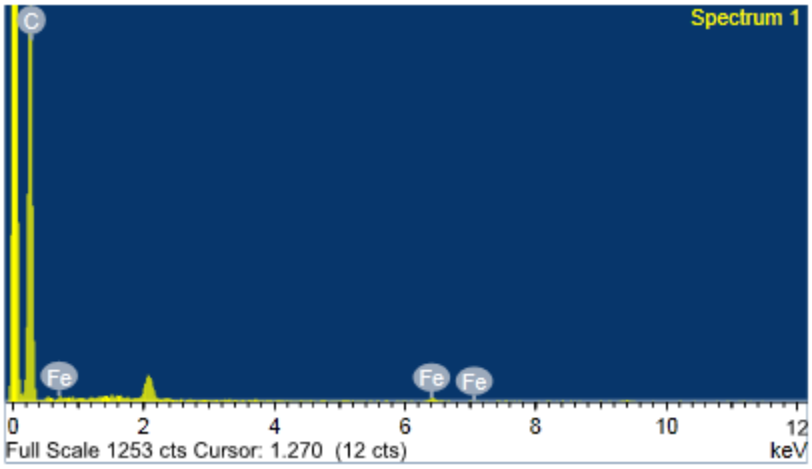

Figure 4.5 EDS for iron carbide impregnated CNTs

Table 4.1 Weight percentages of elements in CNTs prepared (EDS)

Type of Adsorbent	Carbon	Metallic Element	Oxygen
Pure CNTs	96.36	1.14 (Co)	2.40
Iron oxide – CNTs	61.43	15.86	22.71
Silver – CNTs	53.72	17.76	28.52
Aluminium oxide – CNTs	76.34	6.55	17.11
Iron carbide – CNTs	96.36	3.64	-
Silver carbide – CNTs	86.5	12.5	-
Aluminium carbide – CNTs	96	4	-

It can be seen that the weight percentages of all types of CNTs depict the successful impregnation of metal oxides and metal carbides onto the CNTs. Further, the Table shows the exact amounts of metallic elements present in the specific samples for each type of CNTs. A clearer picture of the impregnation will be visible when viewing the SEM of these materials.

4.1.3. Scanning electron microscopy (SEM) of CNTs

In order to study the surface morphology and topography of the CNTs prepared, SEM was conducted for each type of CNTs synthesized. SEM was conducted at different magnifications as provided by the equipment. Samples were first coated by platinum and then put into the SEM microscope chamber where the samples were magnified and analyzed. The results of SEM are shown in the Figures 4.6 – 4.12.

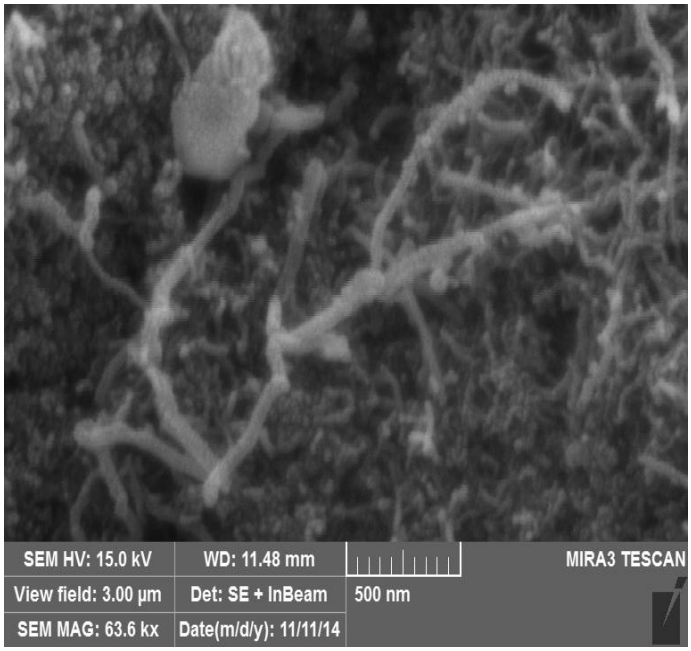

Figure 4.6 SEM for pure CNTs

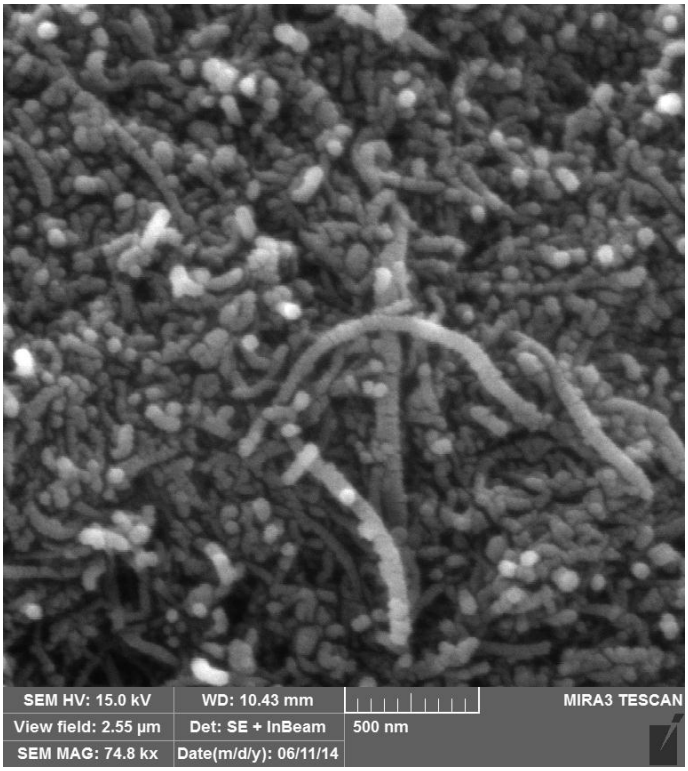

Figure 4.7 SEM for iron oxide impregnated CNTs

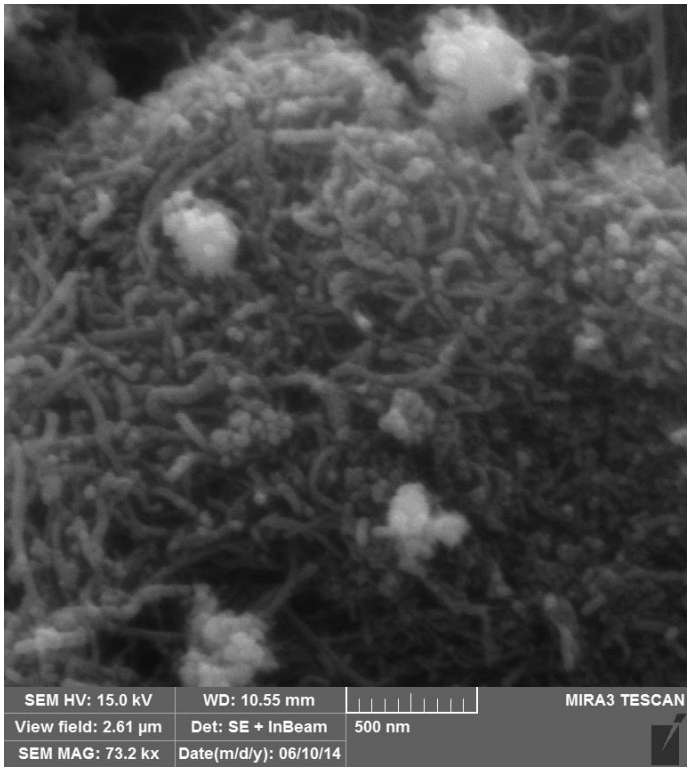

Figure 4.8 SEM for silver impregnated CNTs

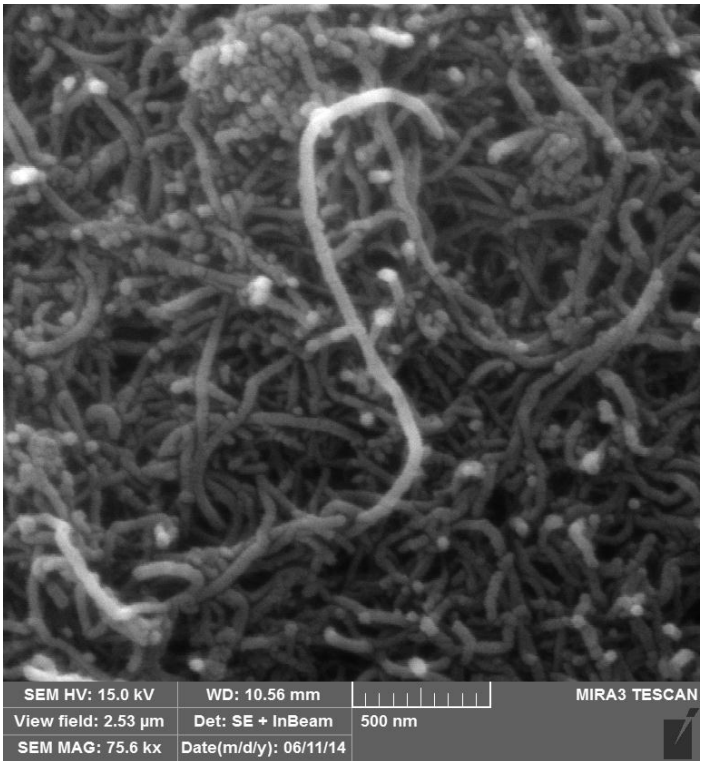

Figure 4.9 SEM for aluminium oxide impregnated CNTs

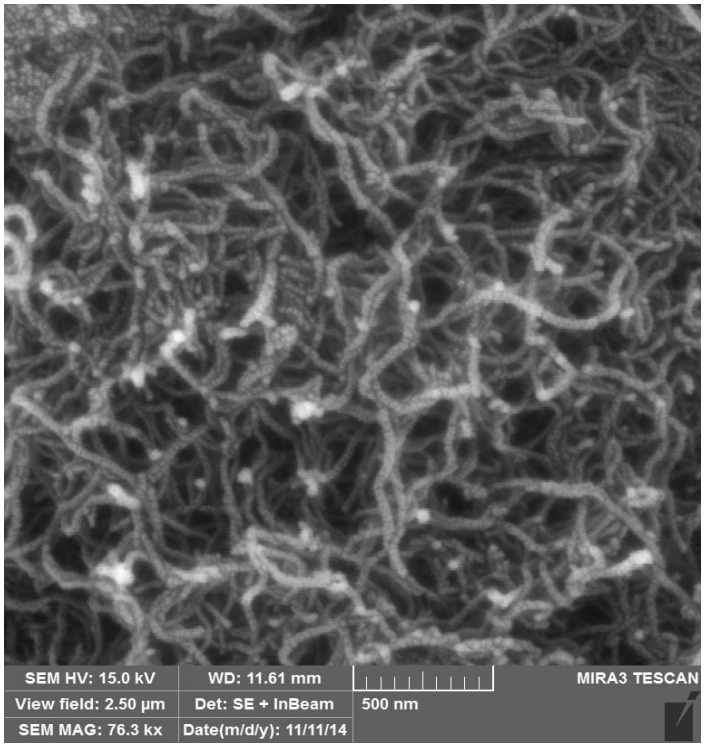

Figure 4.10 SEM for iron carbide impregnated CNTs

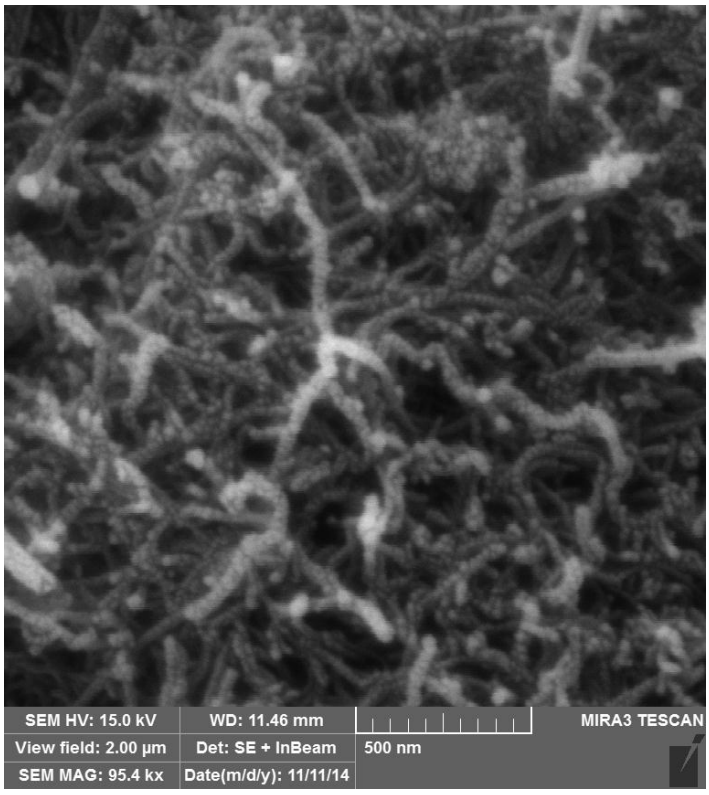

Figure 4.11 SEM for silver carbide impregnated CNTs

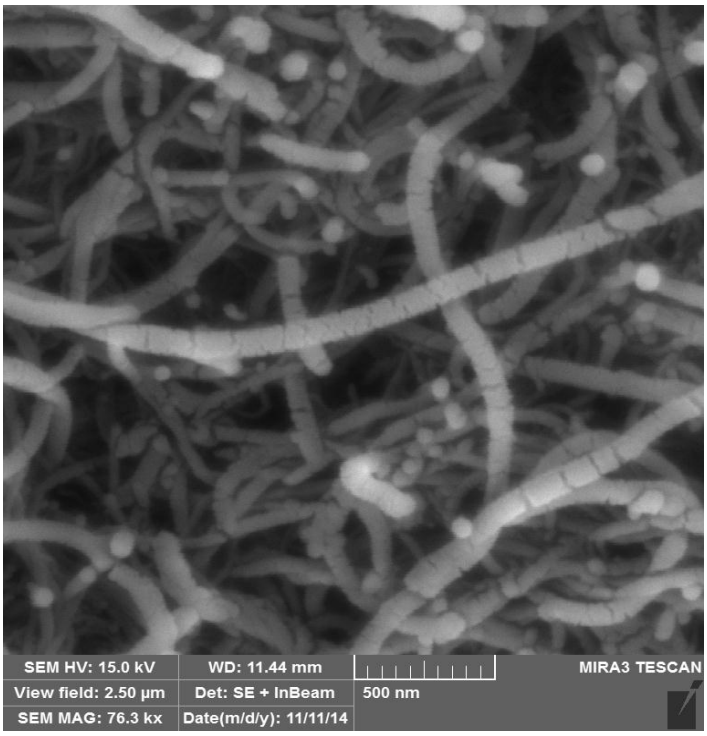

Figure 4.12 SEM for aluminium carbide impregnated CNTs

All the above images from SEM indicate the presence of a type of coating on the tube surface. This is basically the impregnated material either in the form of the metal oxide or metal carbide. For example, the SEM image given in Figure 4.12 shows some cracks on the surface of tubes. These cracks or spaces in fact represent the impregnation at different points of the tubes. It is entirely normal to have these cracks or to have pure tubes in the SEM of impregnated materials because not 100% of the CNTs have been impregnated in each case. On the other hand, Figure 4.6, which represents the image of pure CNTs is devoid of such changes in its surface. The tubes in this image appear to be in cluster form at some places and in isolated form at others.

Due to uneven and non-homogeneous distribution of the impregnated particles, it is difficult to locate these particles on one particular magnification. The magnification of these images is found to be about 7000 times the original size.

4.2. Characterization of Activated Carbon (AC)

AC was also impregnated with metal oxide and metal carbide nano particles like the CNTs and the prepared materials were subjected to TGA, SEM and EDX. The details of characterization of these materials are given in the following paragraphs.

4.2.1. Thermo gravimetric analysis (TGA) of ACs

The conditions of TGA included a temperature of 900°C and the use of air in the furnace. Some material was retained at the end of the experiment depicting the presence of metal oxide and metal carbide particles on the surface of AC. This retention of material in the TGA pan is a clear indication of impurity in the AC which is actually the metal particles.

The decomposition of activated carbon starts taking place at around 500°C according to the plots below. According to the material safety data sheet of activated carbon published by LAWRENCE FACTOR, the ignition temperature of activated carbon is greater than 400°C whereas carbon burns at a maximum of 500°C. The temperature at which silver impregnated AC starts to vanish (450°C) is much lower than those at which the iron oxide and aluminium oxide impregnated AC do (600°C). the reason for this lies in the fact that the melting temperature of silver (910°C) is much lower than those of iron oxide (1600°C) and aluminium oxide (2000°C) [58].

Moreover, the TGA for pure AC is presented inFigure. 4.13whichindicates that the material starts decomposing at around 400 to 425°C. The general trend in change in temperature is observed in the same way as it was in the case of CNTs. Figure 4.13also provides a comparison between the TGA curves of pure AC and aluminium impregnated AC samples.

The curve for 1% impregnated AC and pure AC is found to lie at a lower temperature as compared to the curve of 10% impregnated AC.

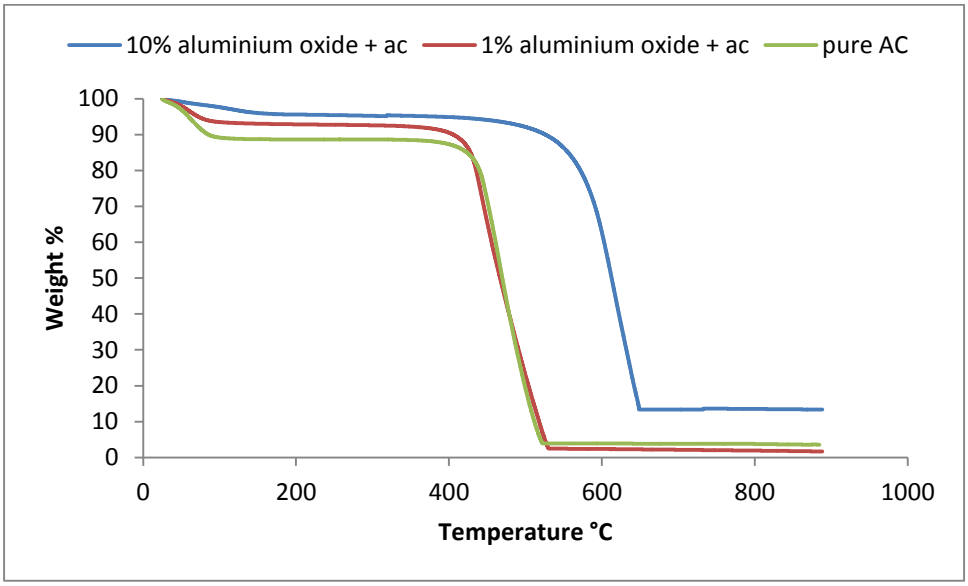

Figure 4.13 TGA comparison (pure AC and aluminium impregnated AC samples)

4.2.2. Energy-dispersive X-ray spectroscopy (EDS) of ACs

EDS or EDX was performed to determine the elements present in the adsorbent materials prepared. The same sample of materials used for SEM were subjected to EDS. The results for the EDS of impregnated samples of AC follow this paragraph. Each peak corresponds to a certain element. The exact percentage of each element in the sample is also tabulated in Table 4.2.

Table 4.2 Weight percentages of elements in AC prepared (EDS)

Type of Adsorbent	Carbon	Metallic Element	Oxygen
Pure AC	86.42	-	13.58
Iron oxide – AC	58.35	20.89	18.03

Silver – AC	82.5	4	13.04
Aluminium oxide – AC	74.06	6.15	15.83
Iron carbide – AC	62.1	19.94	17.69
Silver carbide – AC	69.85	6.95	6.06
Aluminium carbide – AC	61.93	14.56	23.51

4.2.3. Scanning electron microscopy (SEM) of ACs

The surface characteristics of AC samples were done using SEM. After coating samples with platinum metal, they were put into the SEM microscope chamber where they were analyzed at different levels of magnification. The SEM images obtained are shown below.

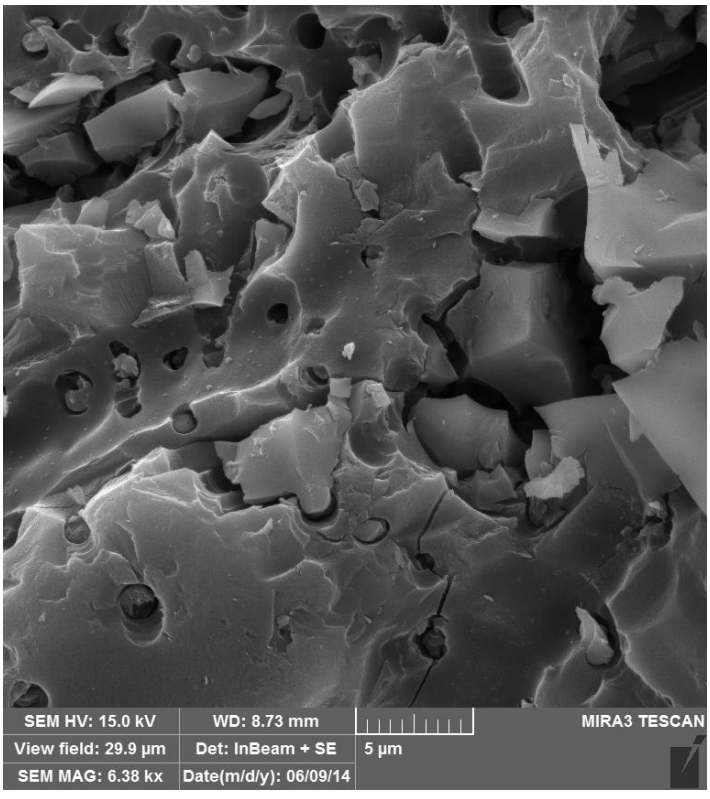

Figure 4.14 SEM for pure AC

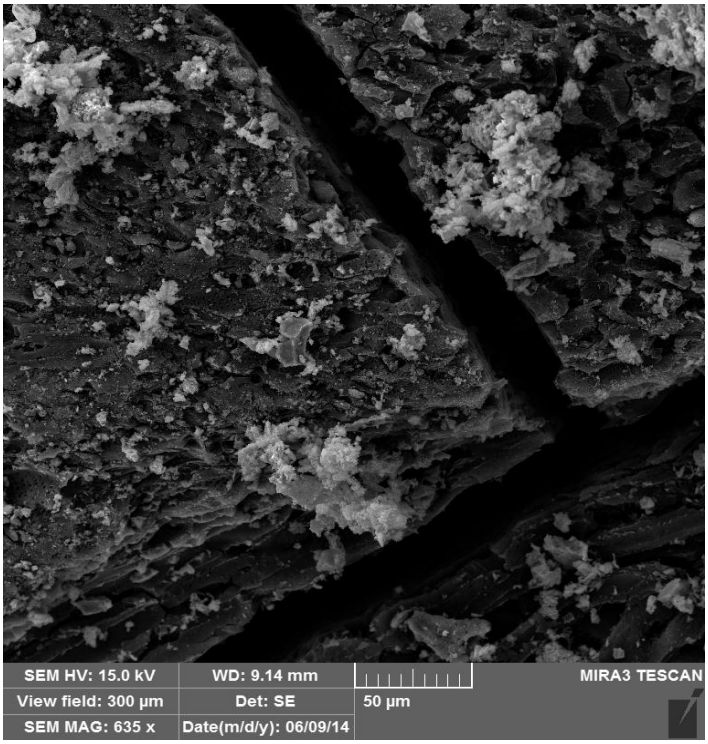

Figure 4.15 SEM for iron oxide impregnated AC

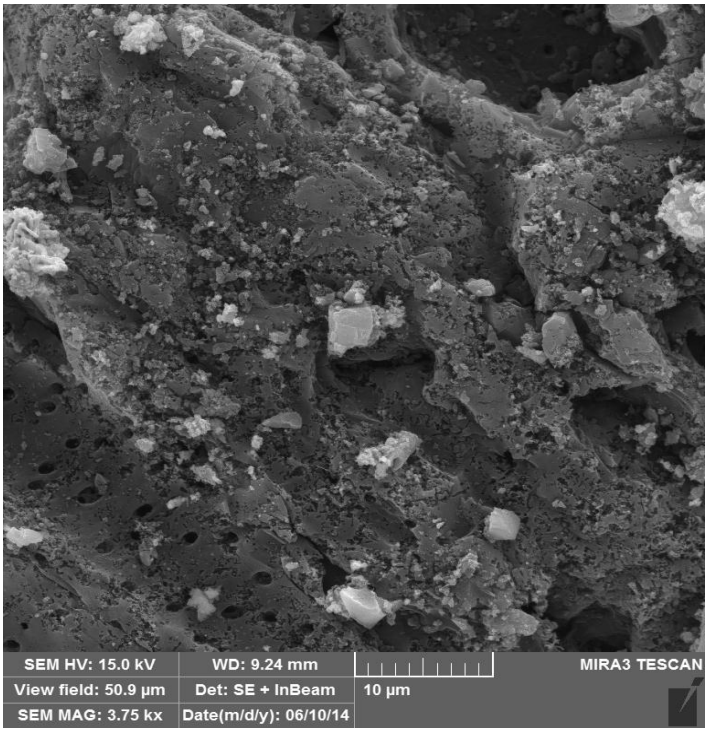

Figure 4.16 SEM for silver impregnated AC

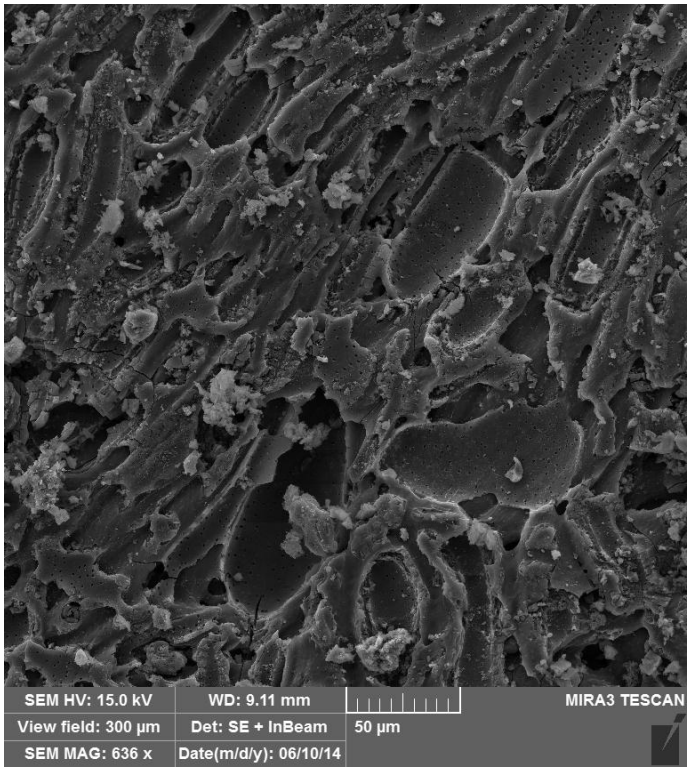

Figure 4.17 SEM for aluminium oxide impregnated AC

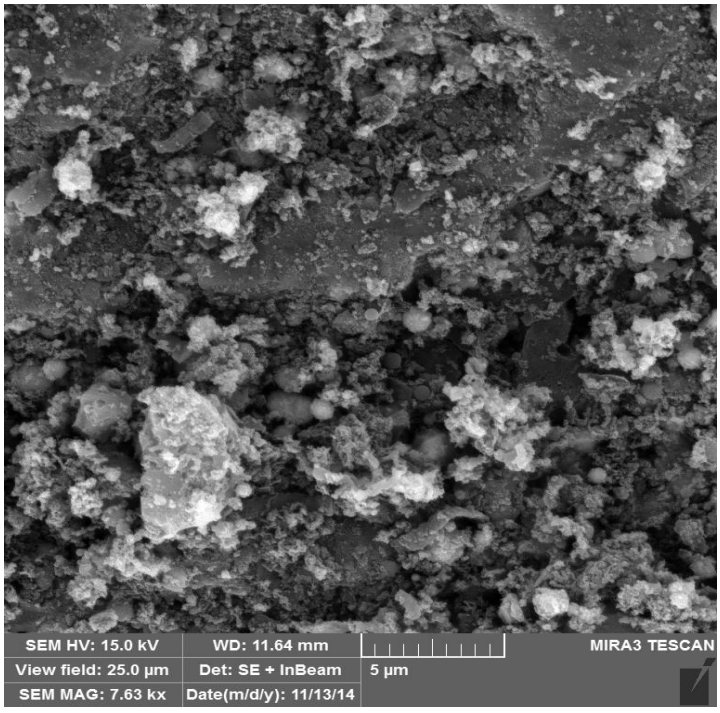

Figure 4.18 SEM for iron carbide impregnated AC

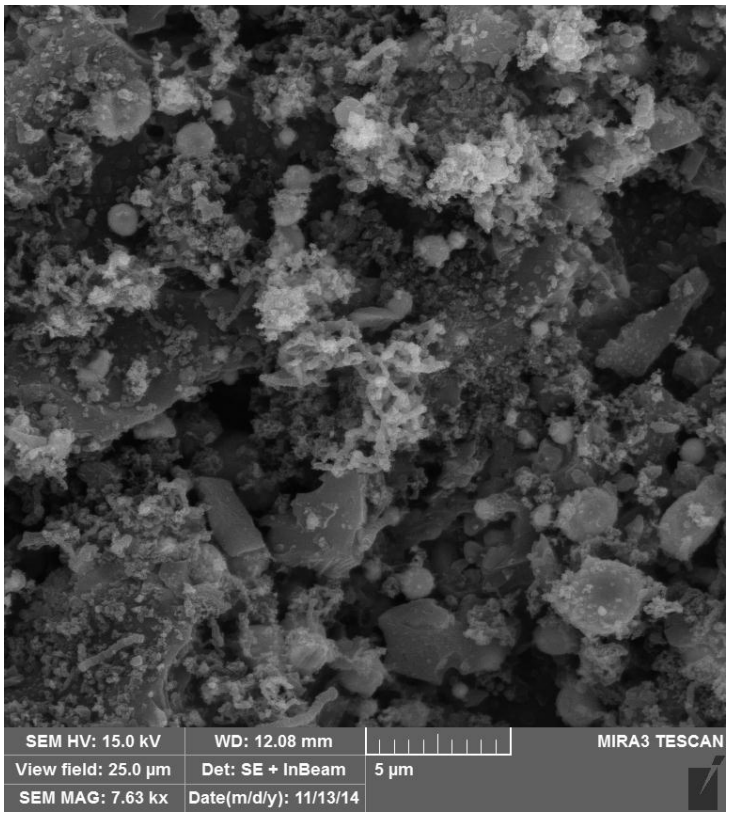

Figure 4.19 SEM for silver carbide impregnated AC

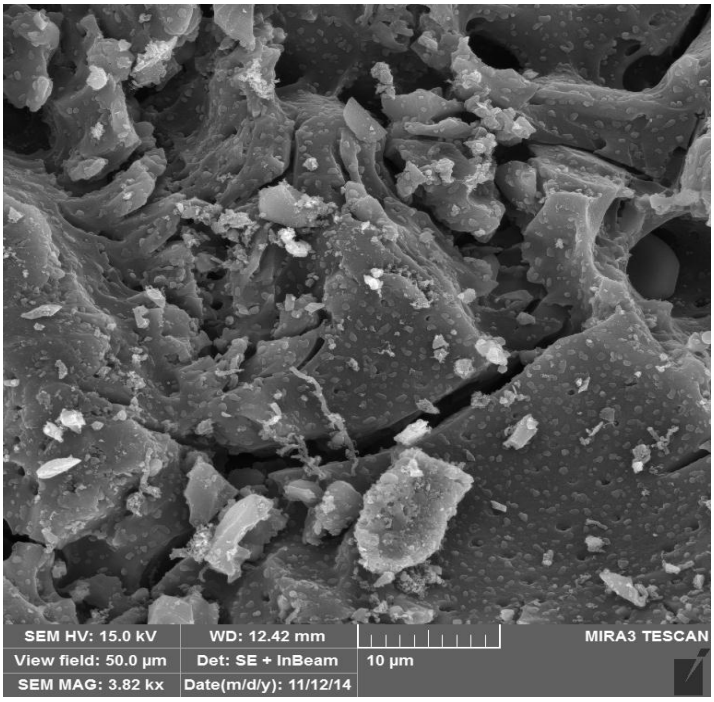

Figure 4.20 SEM for aluminium carbide impregnated AC

Figure 4.14 does not show the impregnated particles presence in the sample. All other SEM images indicate the presence of metal nanoparticles on the surface of AC.

AC, unlike CNTs, is a micro material which is why there is a clear difference between the scale measurements present on the SEM images. The SEM images for AC samples defines a scale of micro meters (microns).

4.3. Removal of Arsenic, Chromium and Lead from Water Using Modified and Non Modified CNTs and AC

The true application of this work is water treatment. More specifically, the different materials (adsorbents) synthesized using CNTs and AC have been used to remove heavy metals (arsenic, chromium and lead) from water. The adsorption of these metal ions onto the adsorbent surface is studied on the basis of their percentage removal each time they are subjected to an adsorbent.

The effect of various factors on the percentage removal is observed and studied. These factors include pH of initial solution, dosage of adsorbent, time of agitation (contact time), speed of agitation and concentration of initial solution. The effects of these parameters will be discussed here.

4.3.1. Removal of Chromium (Cr (VI)) Using Modified and Non Modified CNTs and AC

Different factors affecting the percentage removal of chromium are discussed as below.

4.3.1.1 Effect of pH

The range of pH used for the batch adsorption experiments was from 3 to 8. The results for the percentage removal of chromium have been plotted against the respective pH value of

the initial solution. The maximum removal has been achieved by iron carbide – CNT followed by iron oxide – CNT. At a pH of 6, high values of percentage removal have been seen by all adsorbents. A dropping trend is seen in the case of pure CNTs. This is attributed to the fact that at lower pH values, the surface of CNTs is protonated and at low pH values chromium exists in water in the form of dichromate ions ($Cr_2O_7^{2-}$) [59]. The electrostatic interactions between the adsorbent's positive surface and negative dichromate ions helps in eradication of chromium from water. At higher pH values, the dichromate is converted to its hydroxides and a competition arises between the CrO_4^{2-} ions and the OH- ions for adsorption onto the positive adsorbent surface. This results in a lower removal at higher pH which can be seen by a declining line towards a pH of 8 for each type of adsorbent. Moreover, the metallic oxides have a basic nature which results in protonation of their surface when they are in an aqueous solution of low pH (acidic). This enhances the electrostatic attraction and thus the adsorption of dichromate ions. This is why an impregnated adsorbent is considered to be a multi-site adsorbent. This explains the fact why the removal is greater in case of metal oxide impregnated adsorbents. Although metal carbides are smaller surface area compounds, yet the metal carbide impregnated adsorbents show a good removal of chromium which is attributed to the carbon adsorbent sites.

A similar behavior is seen in the case of activated carbon. The best removal was observed at the lowest pH of 3. As the pH increases, the chemical nature of chromium in water shifts to chromate ion whose adsorption is prevented to a great extent by the hydroxyl ions on limited adsorption sites of the adsorbent. The comparison of AC and CNTs adsorbents suggests that AC gives lower removal than CNTs. This is more of dependent on the size of adsorbate molecules than the pH of solution.

Figures 4.21 to 4.26 represent the results for the removal of chromium with pH variation. Plenty of work has been done regarding the effect of pH on the removal of heavy metals from water. Chromium (VI) was removed using different types of activated carbon and the effect of pH was studied on the removal. For the activated carbon obtained from coconut shells, the adsorption capacity increased from 4.21 to 20.98 mg/g with a decrease in pH from 4 to 2. This happened because at lower pH the surface of AC was protonated and it became ideal for dichromate ion to be attracted towards the adsorbent [52]. Muataz studied the effect of pH on the removal of trivalent chromium and found that the percentage removal increased from pH 5 to 7 from 4 to 10%. This increase was again attributed to the deprotonation of the adsorbent surface at higher pH values. Because chromium ions were present in their free cationic form, they were adsorbed on the negative surface and percentage removal increased [35].

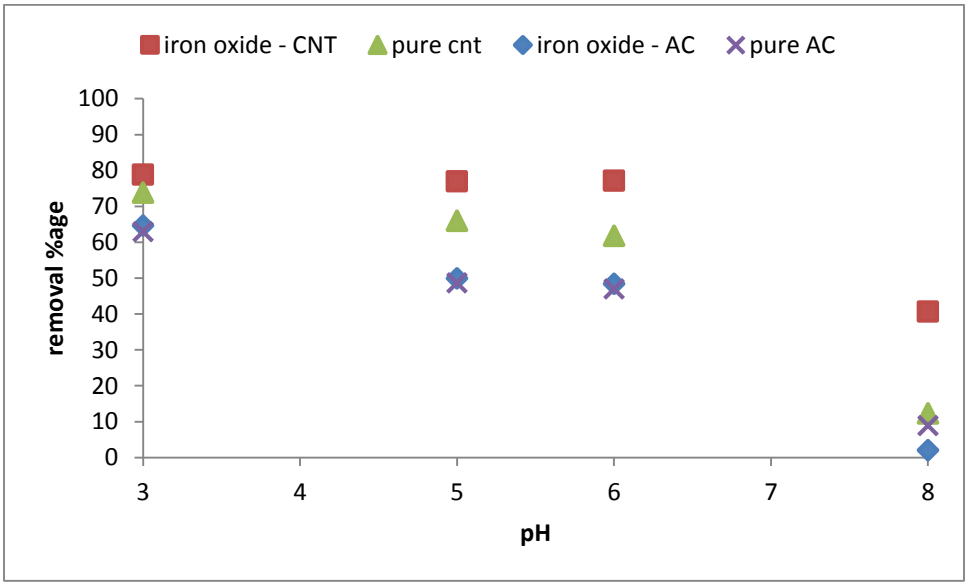

Figure 4.21 Effect of pH on percentage removal of chromium using pure and iron oxide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, adsorbent dosage = 200 mg, time = 2 hrs)

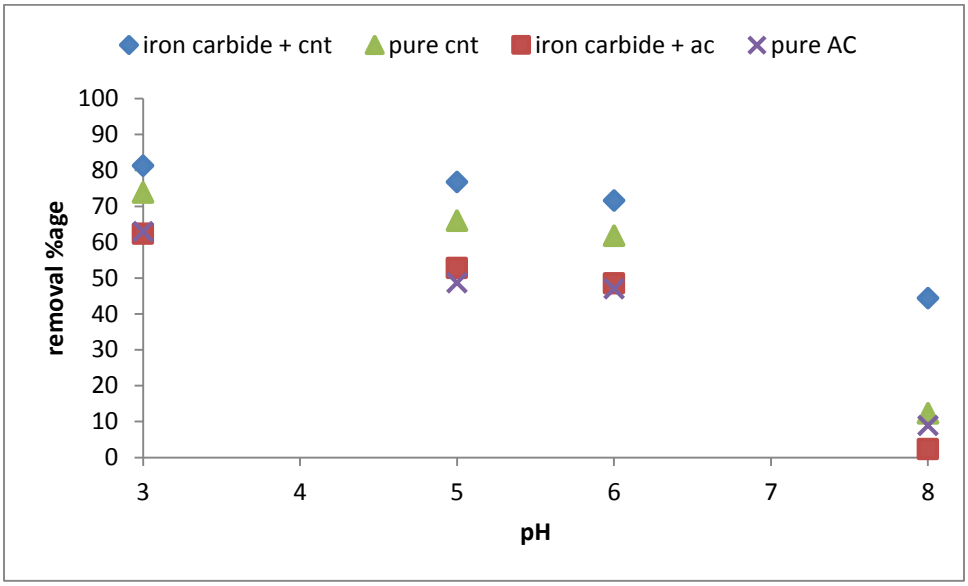

Figure 4.22 Effect of pH on percentage removal of chromium using pure and iron carbide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, adsorbent dosage = 200 mg, time = 2 hrs)

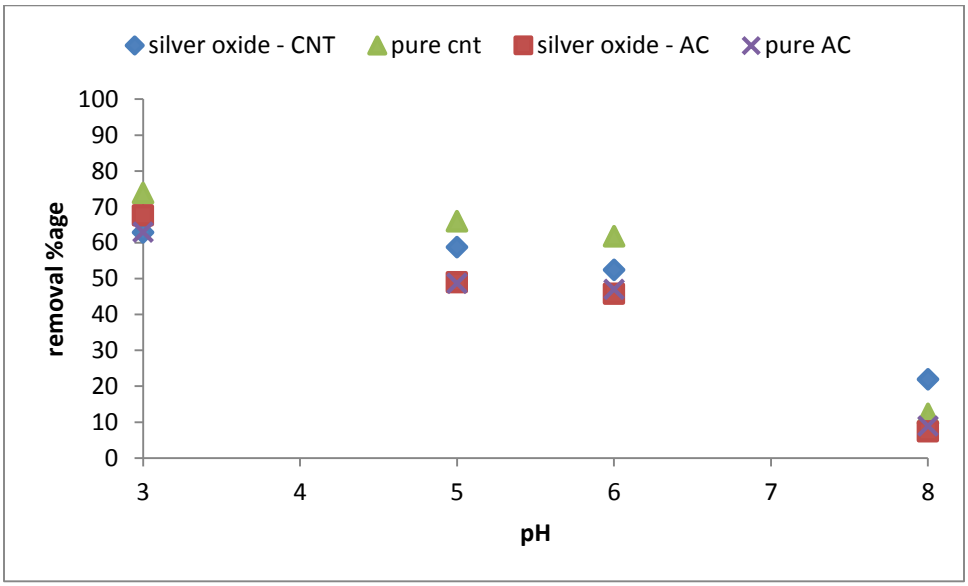

Figure 4.23 Effect of pH on percentage removal of chromium using pure and silver impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, adsorbent dosage = 200 mg, time = 2 hrs)

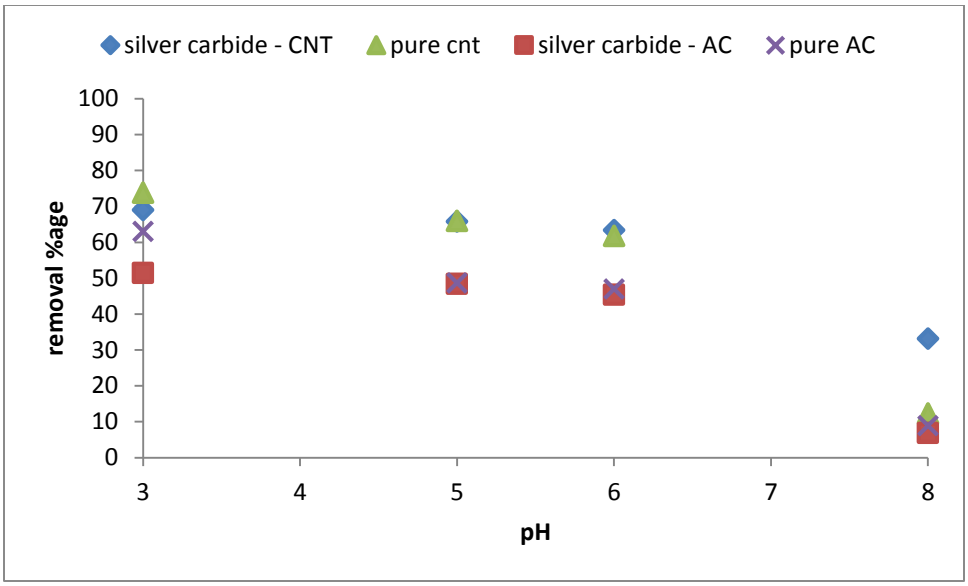

Figure 4.24 Effect of pH on percentage removal of chromium using pure and silver carbide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, adsorbent dosage = 200 mg, time = 2 hrs)

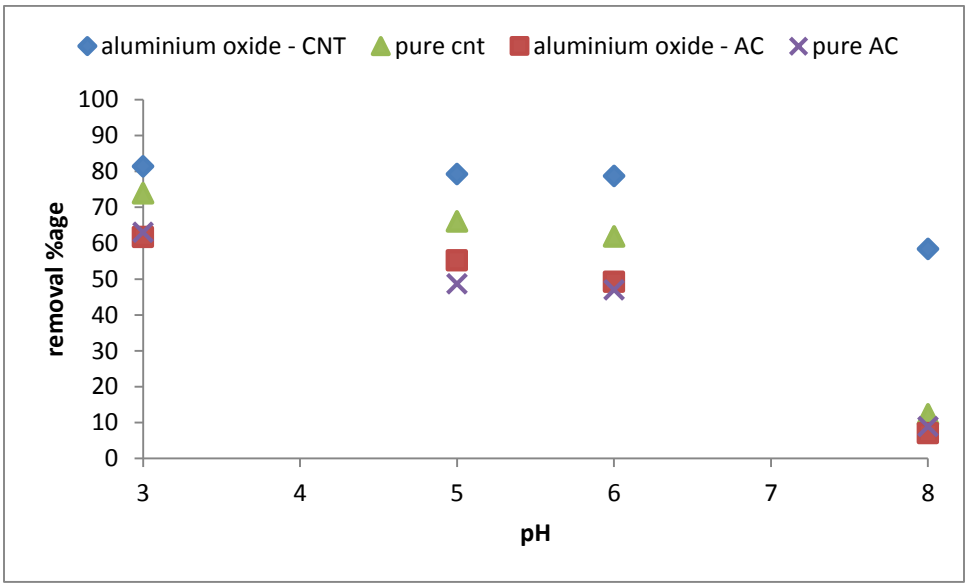

Figure 4.25 Effect of pH on percentage removal of chromium using pure and aluminium oxide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, adsorbent dosage = 200 mg, time = 2 hrs)

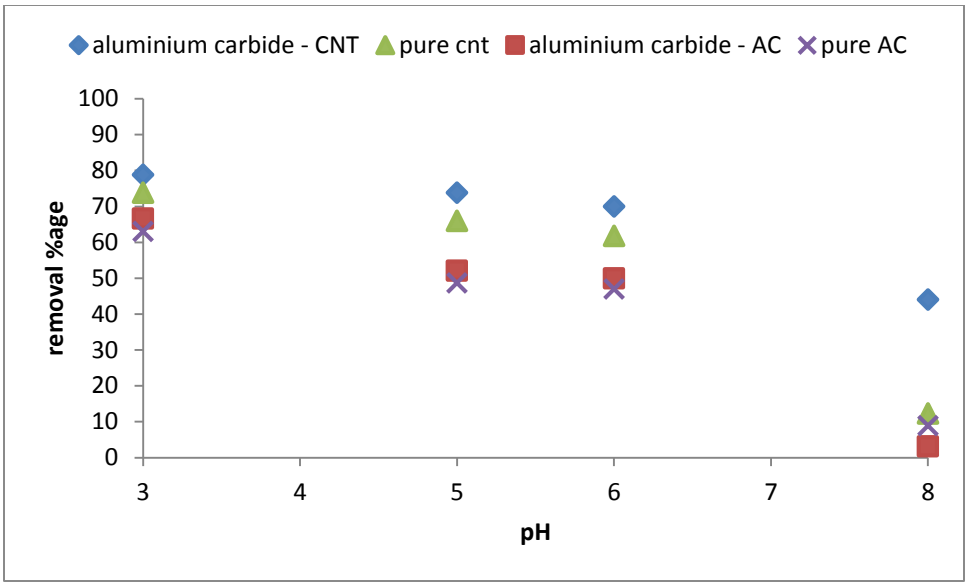

Figure 4.26 Effect of pH on percentage removal of chromium using pure and aluminium carbide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, adsorbent dosage = 200 mg, time = 2 hrs)

4.3.1.2. Effect of Adsorbent Dosage

To observe the effect of dosage on the removal of chromium from water, three different values of dosage were used. These values were 50 mg, 150 mg and 200 mg. Figures 4.27 to 4.32 depict the results for dosage variations for different adsorbents. During these batch experiments, the other parameters were kept constant in order to strive for the best possible value for adsorbent dosage depending on the removal percentage. With an increase in dosage, an increase in the removal percentage was observed. This increase can be explained by the increasing number of adsorption sites (due to increase in quantity of adsorbent) for the same concentration of metallic ions.

Clearly, the impregnated adsorbents seem to give better and efficient results compared to their pure counterparts. With 200 mg of adsorbent dosage, a huge removal of 97.8% is

achieved using iron oxide impregnated CNTs. Moreover, with the use of multi walled CNTs, there is every possible chance of adsorption in the spaces between the concentric tubes. Increasing the amount of CNTs will increase the number of portions where the contaminant can be attracted to. Similarly, increase in the number of micro pores of AC will provide much greater opportunities for adsorption reducing the constraint of molecular size of the adsorbate specie.

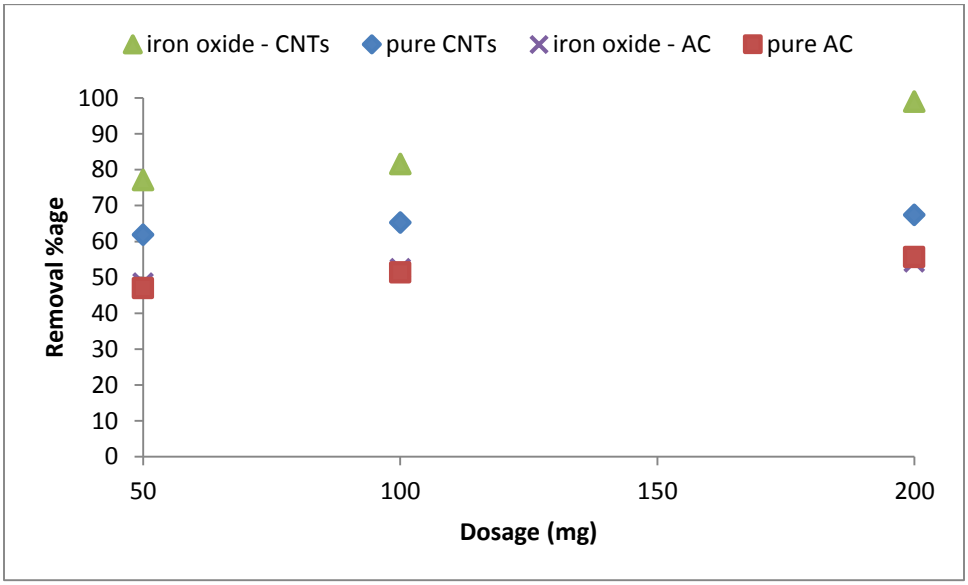

Figure 4.27 Effect of dosage on percentage removal of chromium using pure and iron oxide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, time = 2 hrs)

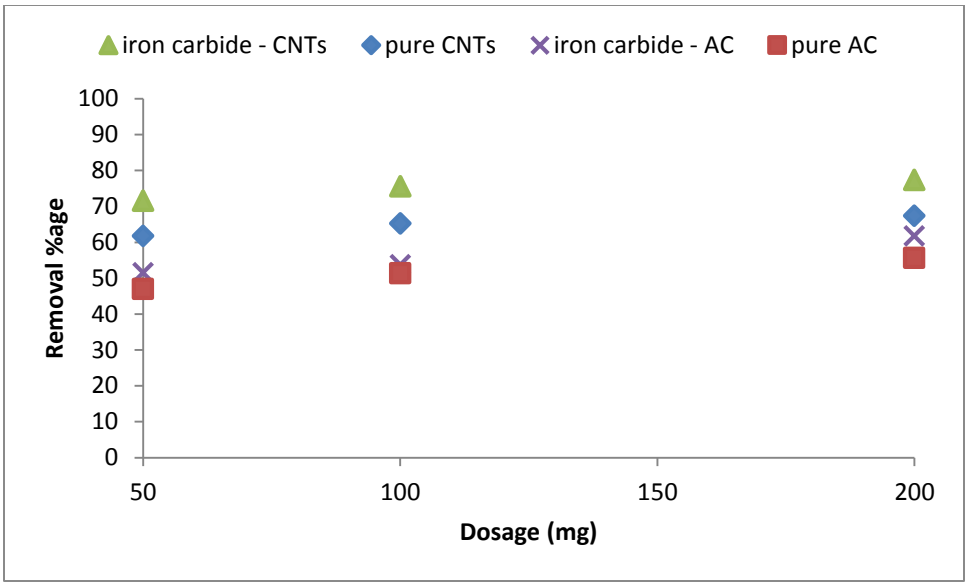

Figure 4.28 Effect of dosage on percentage removal of chromium using pure and iron carbide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, time = 2 hrs)

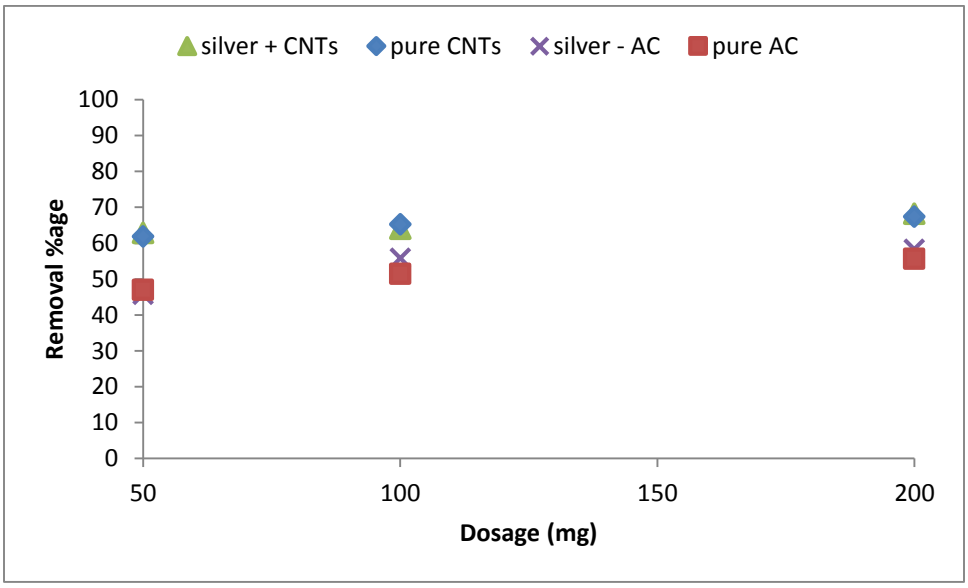

Figure 4.29 Effect of dosage on percentage removal of chromium using pure and silver impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, time = 2 hrs)

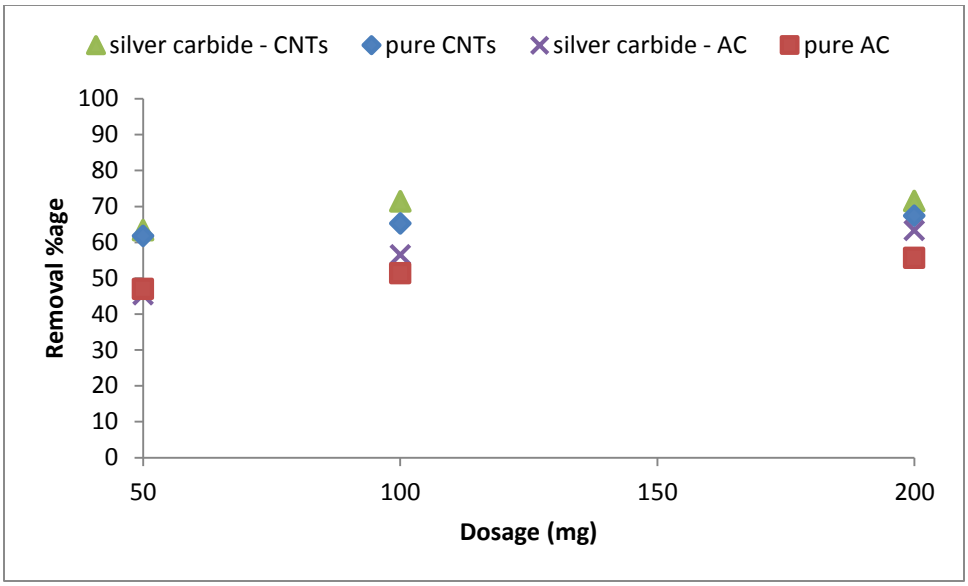

Figure 4.30 Effect of dosage on percentage removal of chromium using pure and silver carbide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, time = 2 hrs)

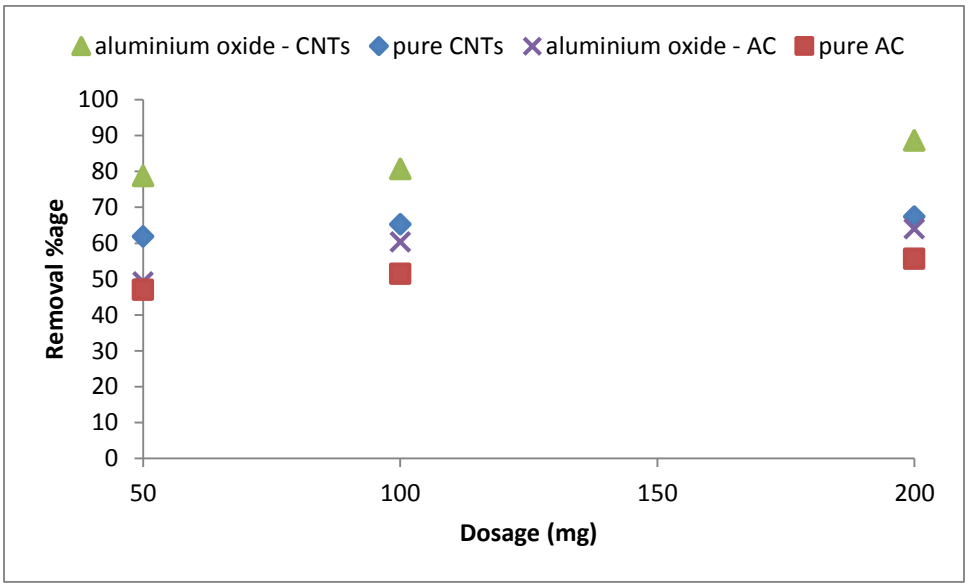

Figure 4.31 Effect of dosage on percentage removal of chromium using pure and aluminium oxide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, time = 2 hrs)

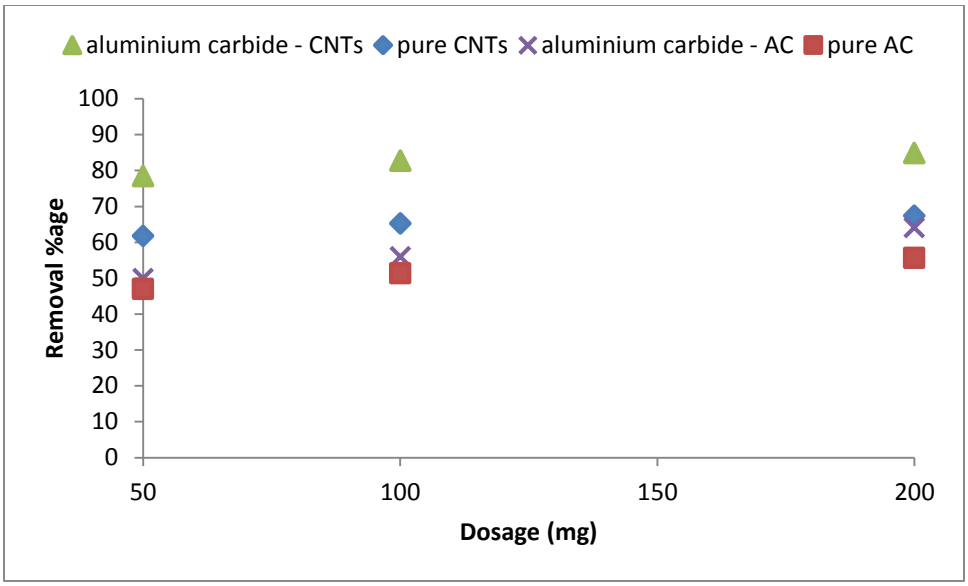

Figure 4.32 Effect of dosage on percentage removal of chromium using pure and aluminium carbide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, time = 2 hrs)

4.3.1.3 Effect of Contact Time (Agitation Time)

Five different time intervals were selected to study the effect of contact time on the removal of chromium. As time increased, the adsorption of chromium increased for each adsorbent. Majority of the times, equilibrium was reached at about 4 to 5 hours of agitation time. This accounts for the saturation of adsorption sites on the adsorbents. The same fixed concentration of chromium (1 ppm) was used but with the increment in time, adsorption increased until the adsorbents were exhausted. The maximum removal (almost 100%) was achieved by iron oxide and aluminium oxide impregnated CNTs. This removal was obtained at 4 hours of time and it remained constant for another one hour to indicate the condition of equilibrium.

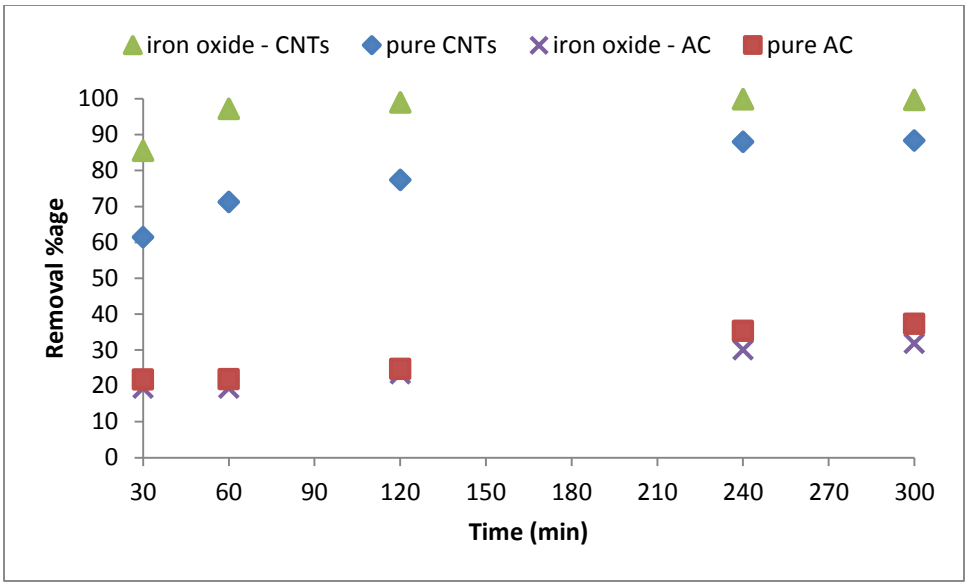

Figure 4.33 Effect of contact time on percentage removal of chromium using pure and iron oxide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, dosage = 200 mg)

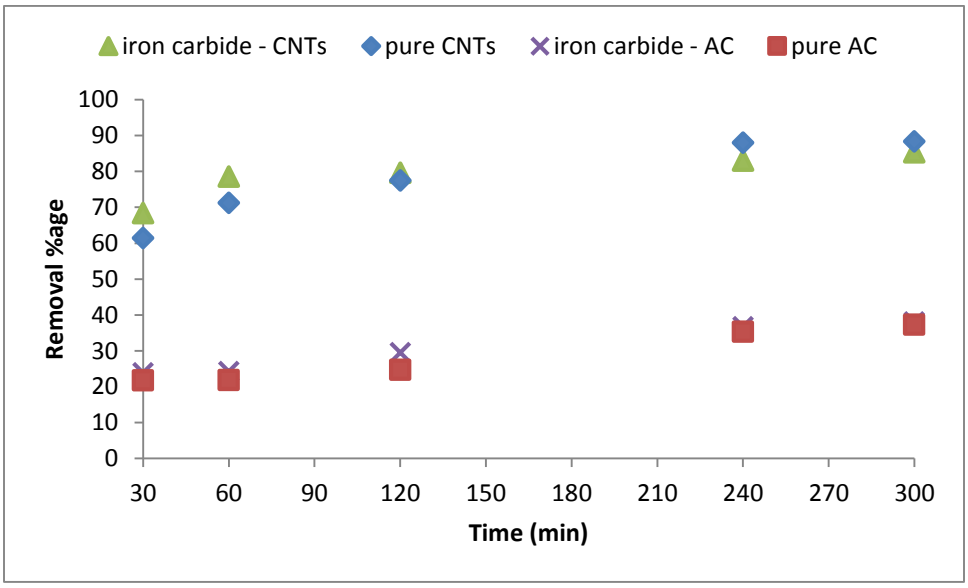

Figure 4.34 Effect of contact time on percentage removal of chromium using pure and iron carbide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, dosage = 200 mg)

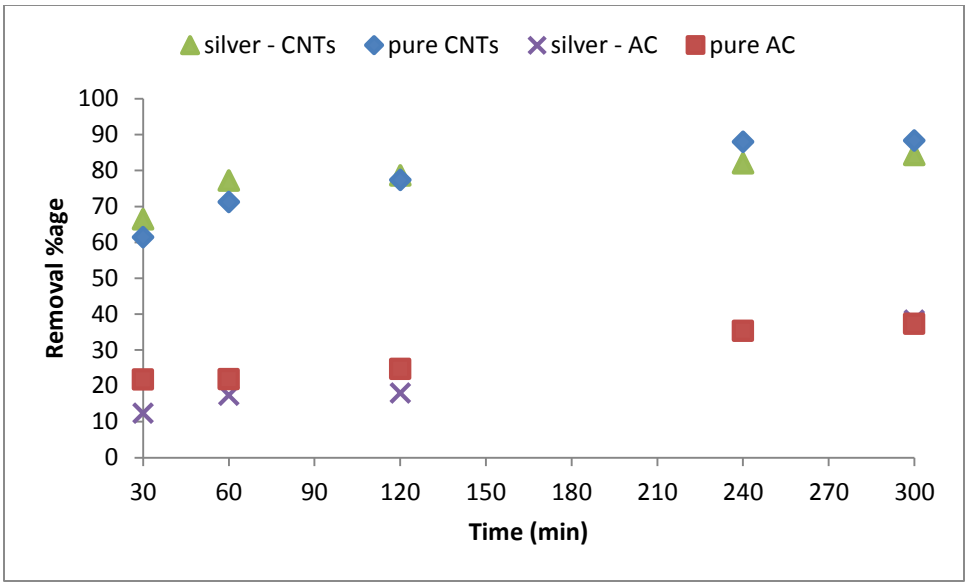

Figure 4.35 Effect of contact time on percentage removal of chromium using pure and silver impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, dosage = 200 mg)

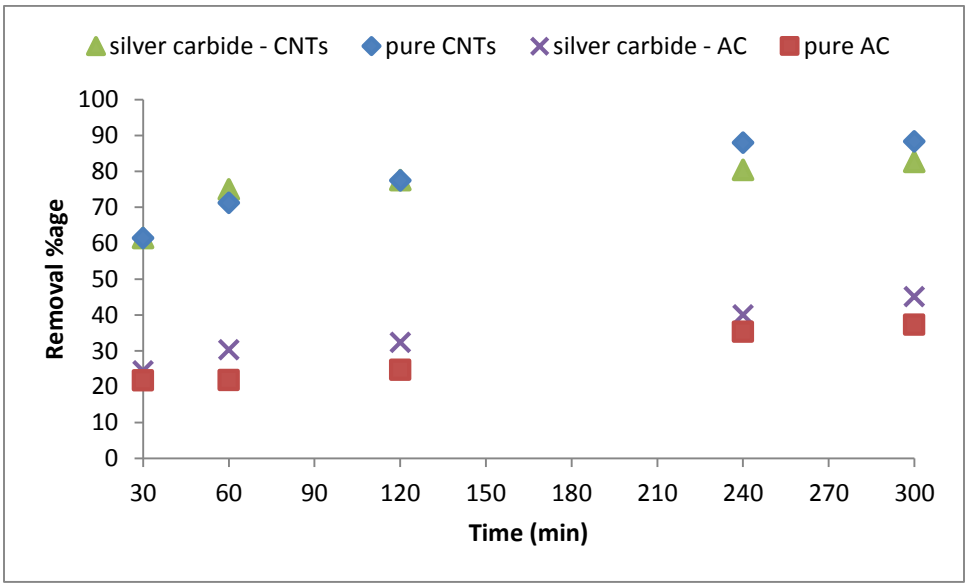

Figure 4.36 Effect of contact time on percentage removal of chromium using pure and silver carbide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, dosage = 200 mg)

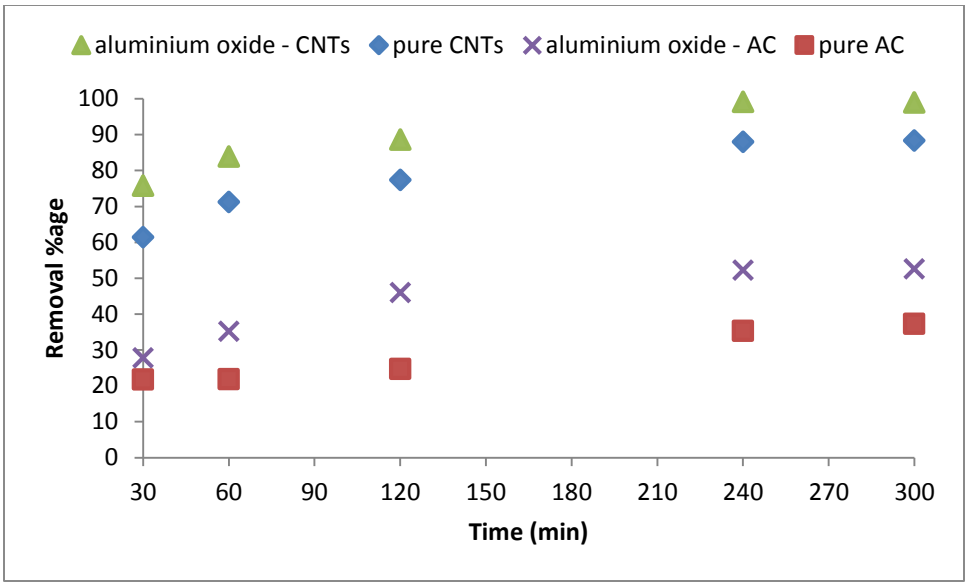

Figure 4.37 Effect of contact time on percentage removal of chromium using pure and aluminium oxide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, dosage = 200 mg)

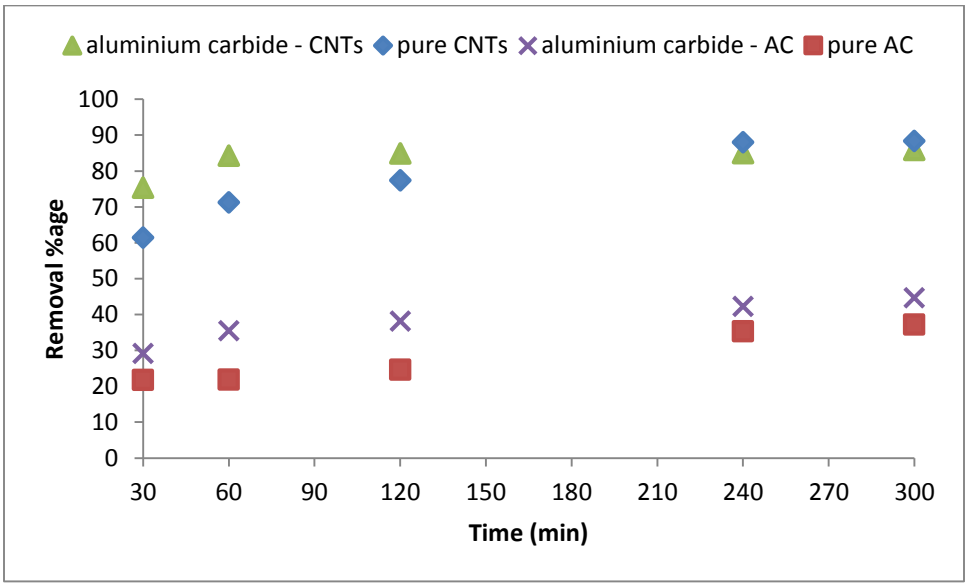

Figure 4.38 Effect of contact time on percentage removal of chromium using pure and aluminium carbide impregnated CNTs and AC (initial conc. = 1 ppm, agitation speed = 200 rpm, pH = 6, dosage = 200 mg)

4.3.1.4 Effect of Agitation Speed

The effect of agitation speed was observed using three different speeds of the lab shaker. Figures 4.39 to 4.44 represent the respective results. With an increase in the agitation speed, the diffusion of metal ions becomes more effective and the external mass transfer effects

are reduced to a great extent [35]. This fast rate of mass transfer results in high adsorption and ultimately an increase in the removal of chromium from water.

Ihsanullah carried out the removal of hexavalent chromium using acid modified CNTs and AC and he has found a gradual increase in adsorption and reported the results based on the fact that external mass transfer resistance was reduced as the speed increases [59]. Similar results were obtained when trivalent chromium was removed using functionalized CNTs. The author reports the results because of an increase in the mass transfer [35]. According to a study the removal of lead was increased from 33 to 39% by increasing the agitation speed from 50 to 150 rpm using carboxylic functionalized CNTs [56].

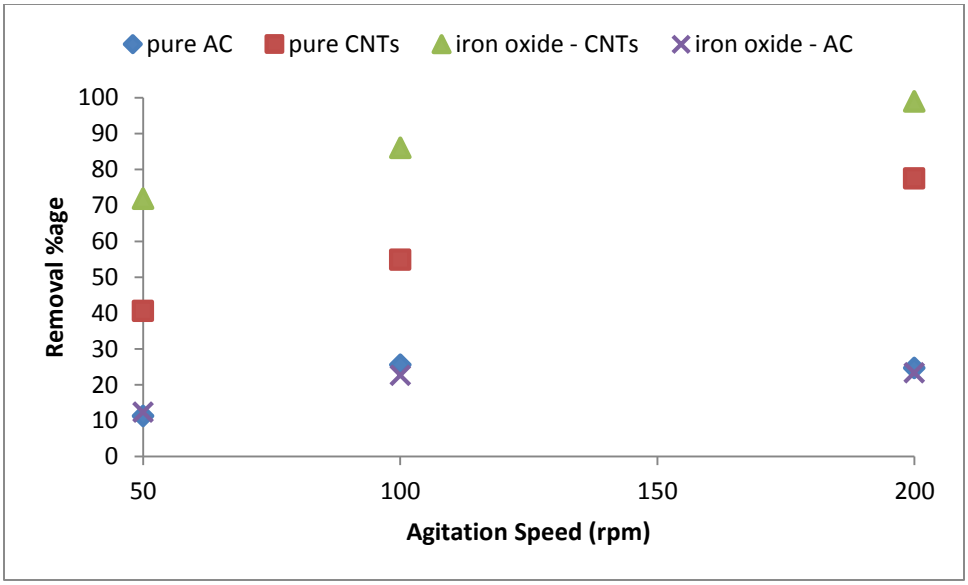

Figure 4.39 Effect of agitation speed on percentage removal of chromium using pure and iron oxide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, pH = 6, dosage = 200 mg)

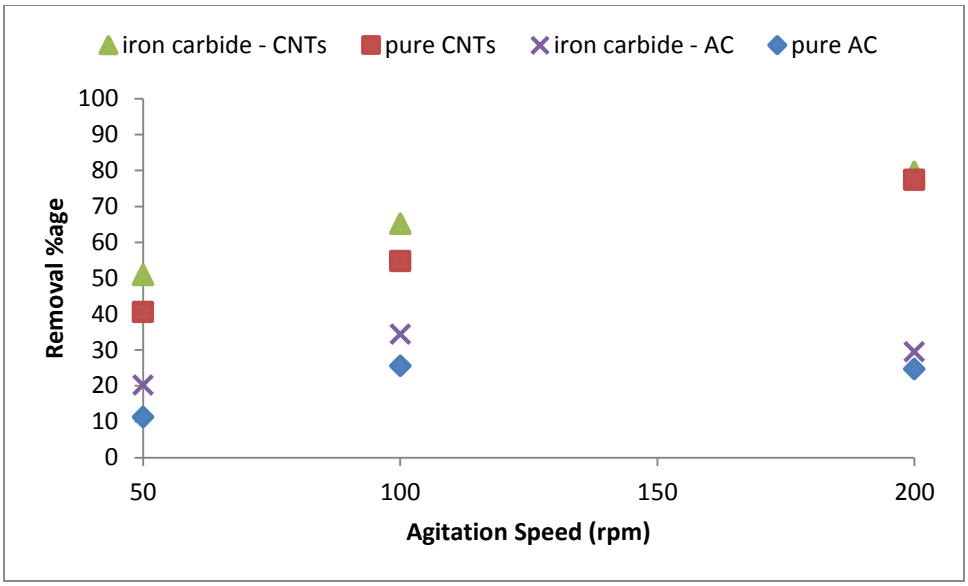

Figure 4.40 Effect of agitation speed on percentage removal of chromium using pure and iron carbide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, pH = 6, dosage = 200 mg)

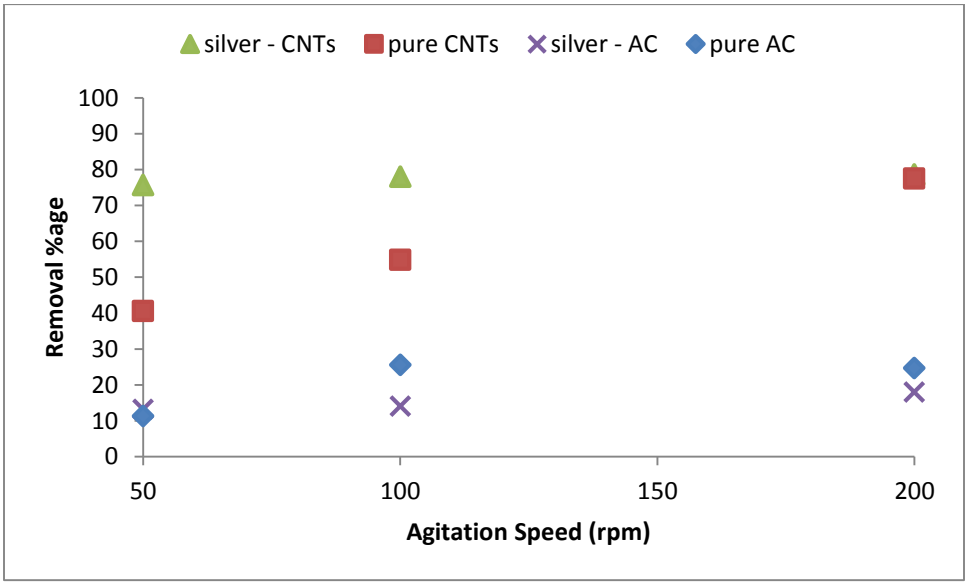

Figure 4.41 Effect of agitation speed on percentage removal of chromium using pure and silver impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, pH = 6, dosage = 200 mg)

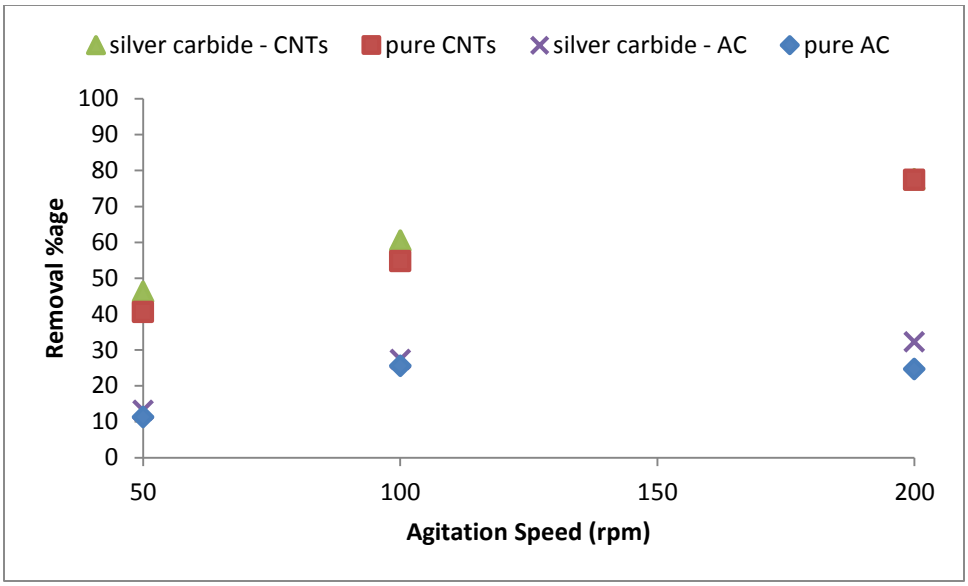

Figure 4.42 Effect of agitation speed on percentage removal of chromium using pure and silver carbide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, pH = 6, dosage = 200 mg)

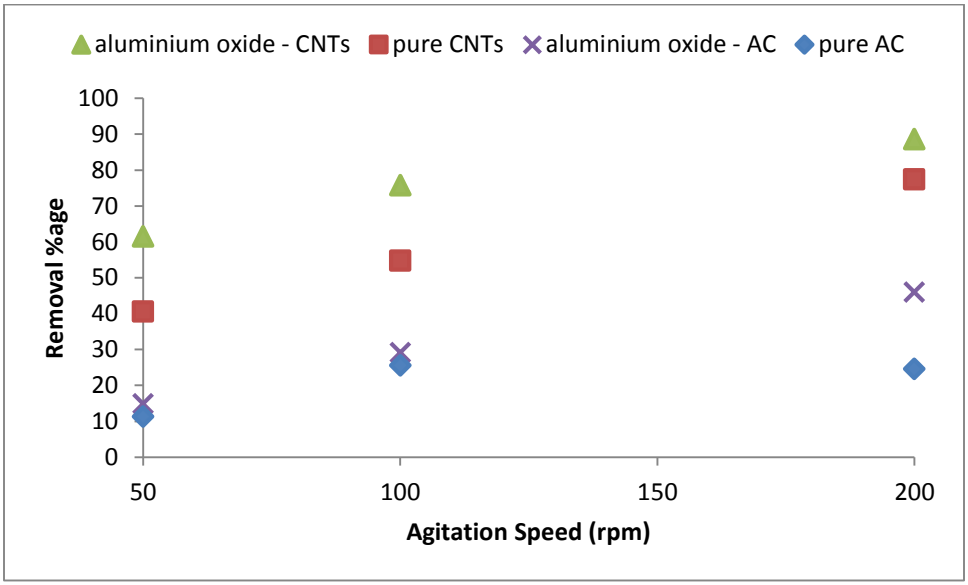

Figure 4.43 Effect of agitation speed on percentage removal of chromium using pure and aluminium oxide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, pH = 6, dosage = 200 mg)

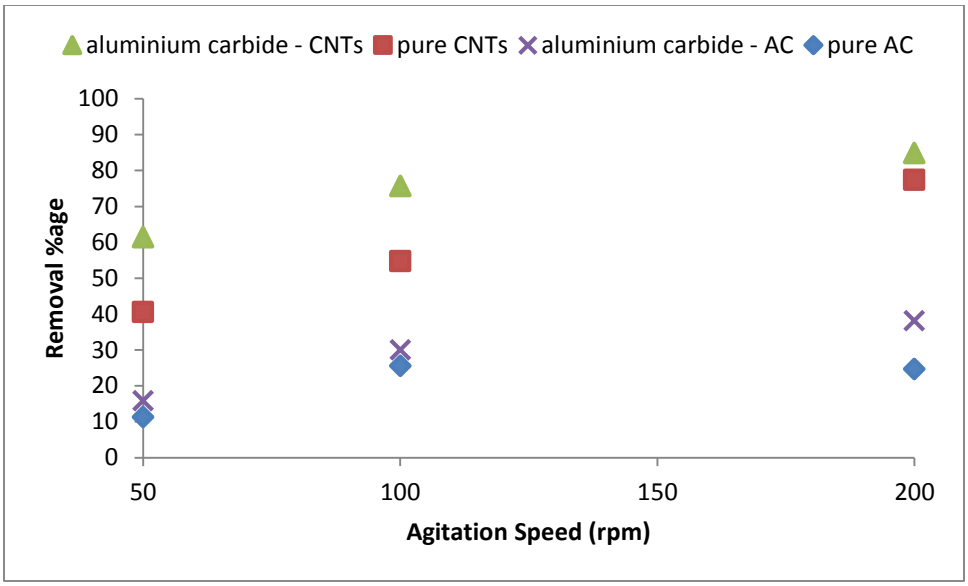

Figure 4.44 Effect of agitation speed on percentage removal of chromium using pure and aluminium carbide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, pH = 6, dosage = 200 mg)

4.3.2. Removal of Arsenic (As^{2+}) Using Modified and Non Modified CNTs and AC

Similar to chromium, various parameters were varied in the batch experiments for arsenic as well. The results for the changing removal percentage are described as follows.

4.3.2.1 Effect of pH

Figures 4.45 to 4.50 represent the results pertaining to the percentage removal of arsenic with variation in pH of the initial aqueous solution. The pH values have been varied from 3 to 8. It can be seen that there is a gradual increase in percentage removal as the pH increases unless in most cases it becomes almost stable. In this pH range, the dominant arsenic specie in water are $H_2AsO_4^-$ and $HAsO_4^{2-}$[55]. The attraction between positive adsorbent surface and the negative ions becomes the cause of arsenic removal.

In case of silver impregnated adsorbents, the percentage removal is low which is attributed to covering of some portion of the adsorbent surface by metal particles disallowing the sorption process after a certain limit [55]. The maximum removal of arsenic is given by

iron impregnated CNTs which is around 80%. The percentage of iron oxide impregnated and its distribution in the CNT matrix has the additional advantage of enhancing the adsorption capabilities of the material.

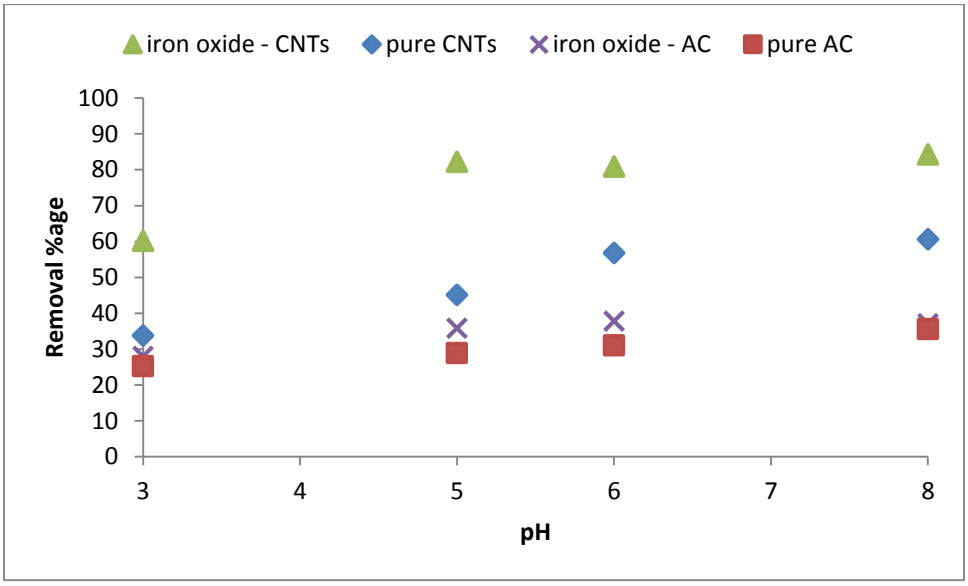

Figure 4.45 Effect of pH on percentage removal of arsenic using pure and iron oxide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, dosage = 50 mg)

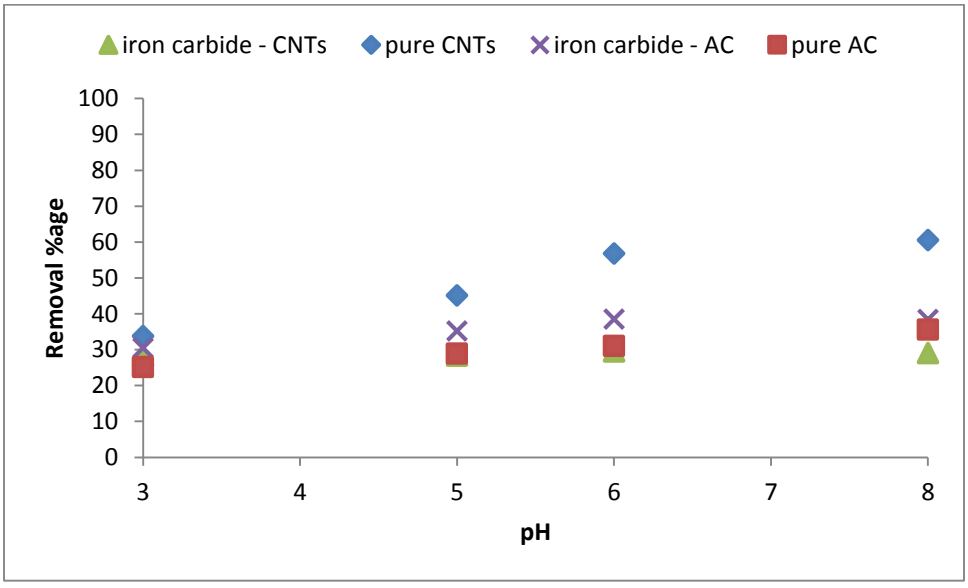

Figure 4.46 Effect of pH on percentage removal of arsenic using pure and iron carbide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, dosage = 50 mg)

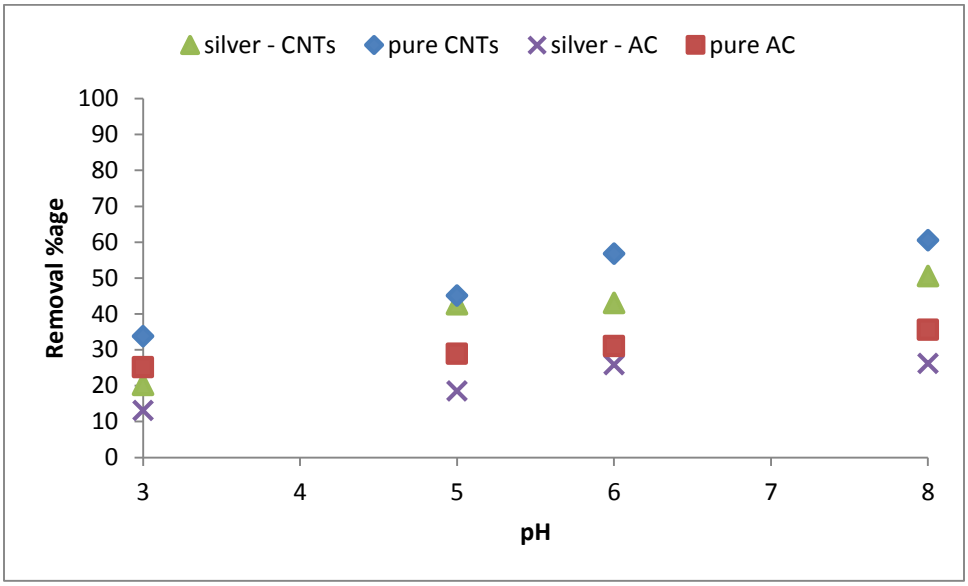

Figure 4.47 Effect of pH on percentage removal of arsenic using pure and silver impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, dosage = 50 mg)

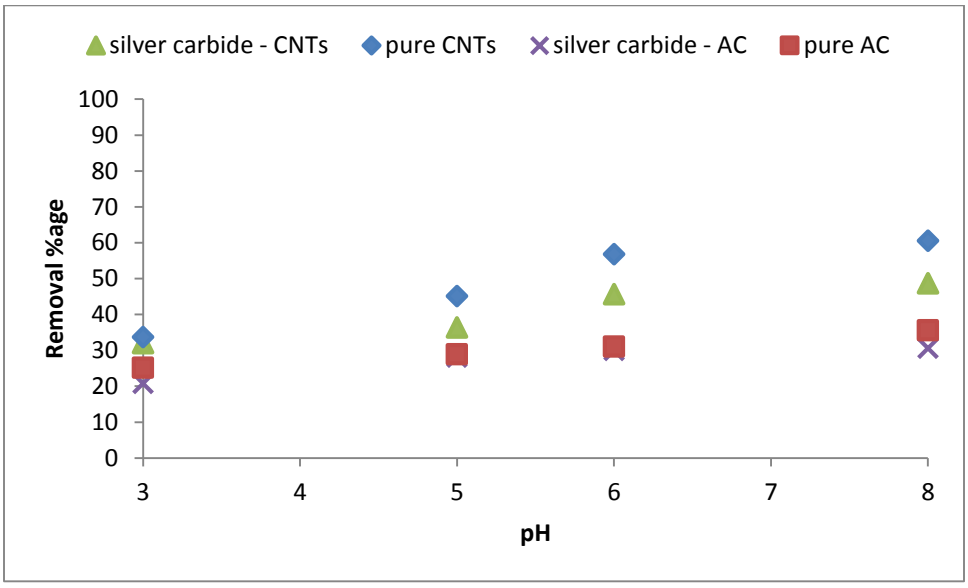

Figure 4.48 Effect of pH on percentage removal of arsenic using pure and silver carbide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, dosage = 50 mg)

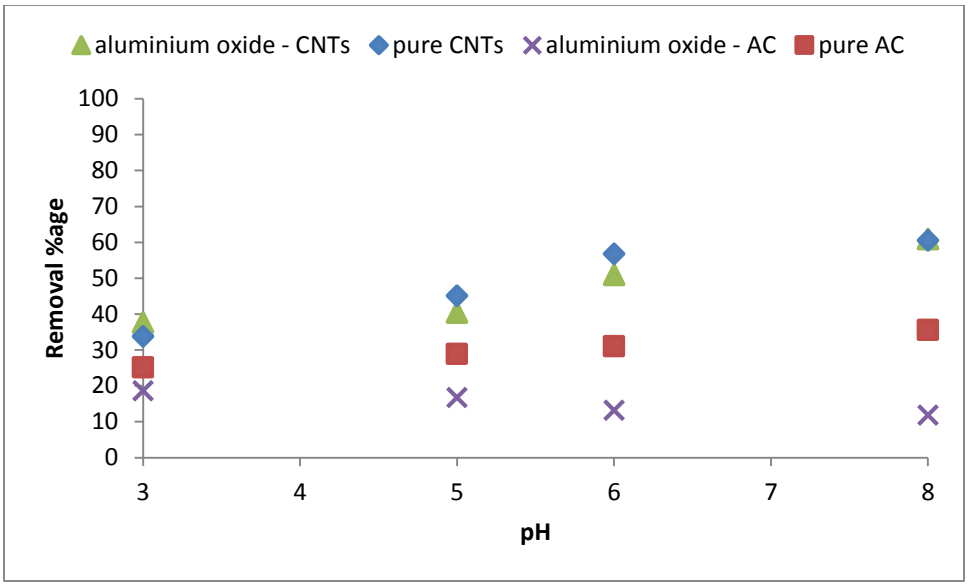

Figure 4.49 Effect of pH on percentage removal of arsenic using pure and aluminium oxide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, dosage = 50 mg)

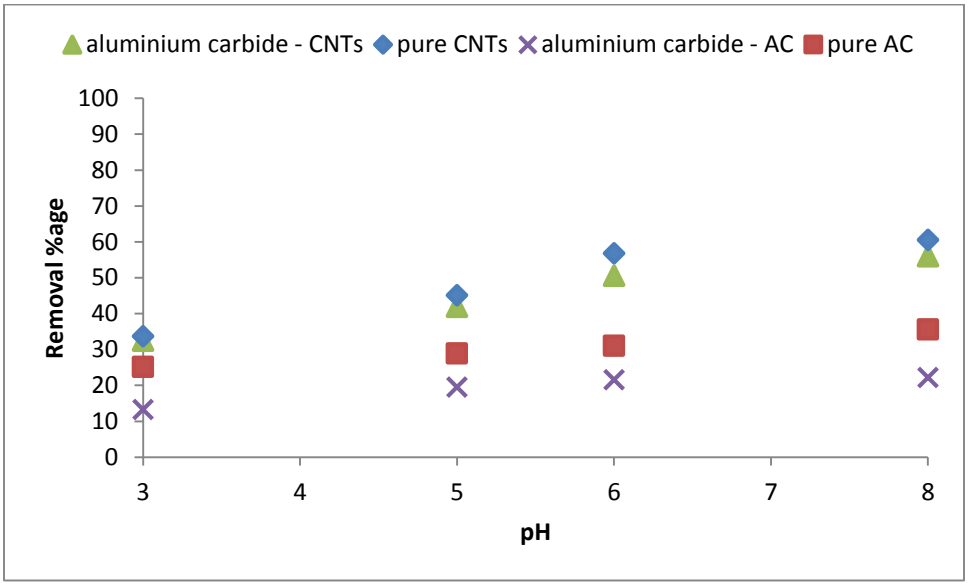

Figure 4.50 Effect of pH on percentage removal of arsenic using pure and aluminium carbide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, dosage = 50 mg)

4.3.2.2 Effect of Adsorbent Dosage

Similar to chromium, for the adsorption of arsenic, three different dosage values were used to study its effect. Figures 4.51 to 4.56 depict the results for dosage variations for different adsorbents. All other parameters were kept constant while dosage was varied to get the best

optimum value. As the concentration remained same each time, a decline in the removal percentage is seen which is attributed to the decrease in adsorption sites as the experiment proceeds.

Iron oxide impregnated CNTs perform around 100% when the dosage is raised to a maximum of 200 mg. Similarly, the results for silver impregnated CNTs show a removal percentage of around more than 90%. With the use of multi walled CNTs, there is every possible chance of adsorption in between the concentric tubes. Increasing the amount of CNTs will increase the number of portions where the contaminant can be attracted to. Similarly, increase in the number of micro pores of AC will provide much greater opportunities for adsorption reducing the constraint of molecular size of the adsorbate specie.

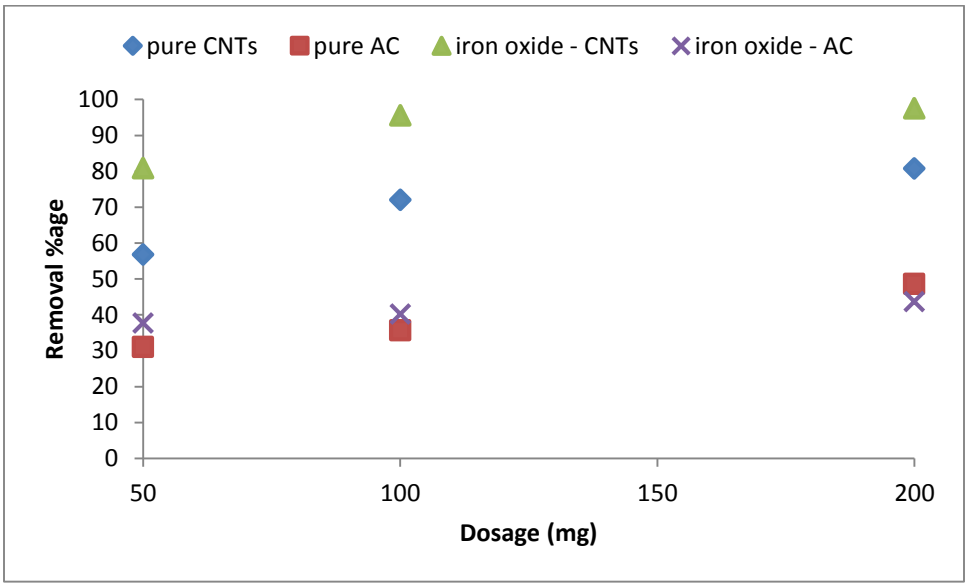

Figure 4.51 Effect of adsorbent dosage on percentage removal of arsenic using pure and iron oxide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, pH = 6)

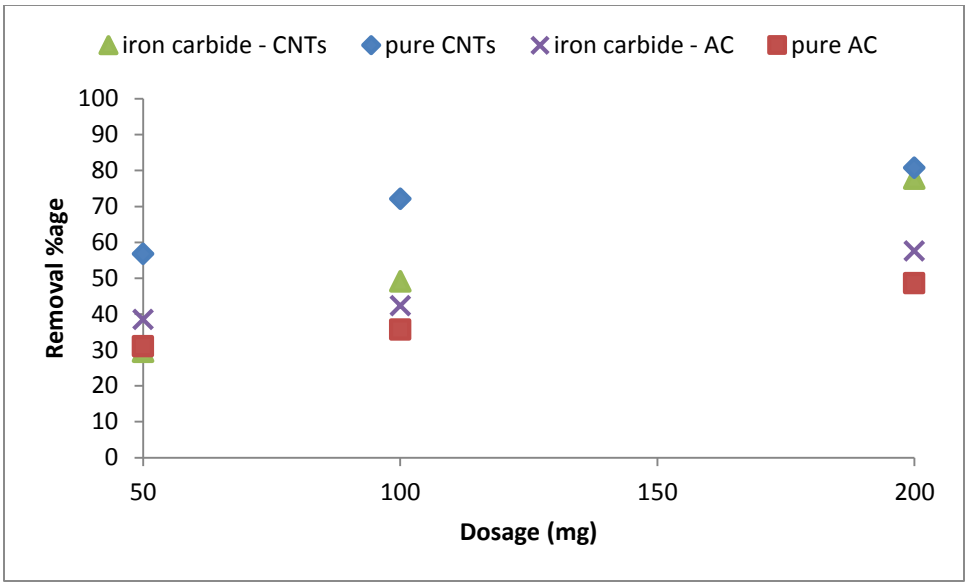

Figure 4.52 Effect of adsorbent dosage on percentage removal of arsenic using pure and iron carbide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, pH = 6)

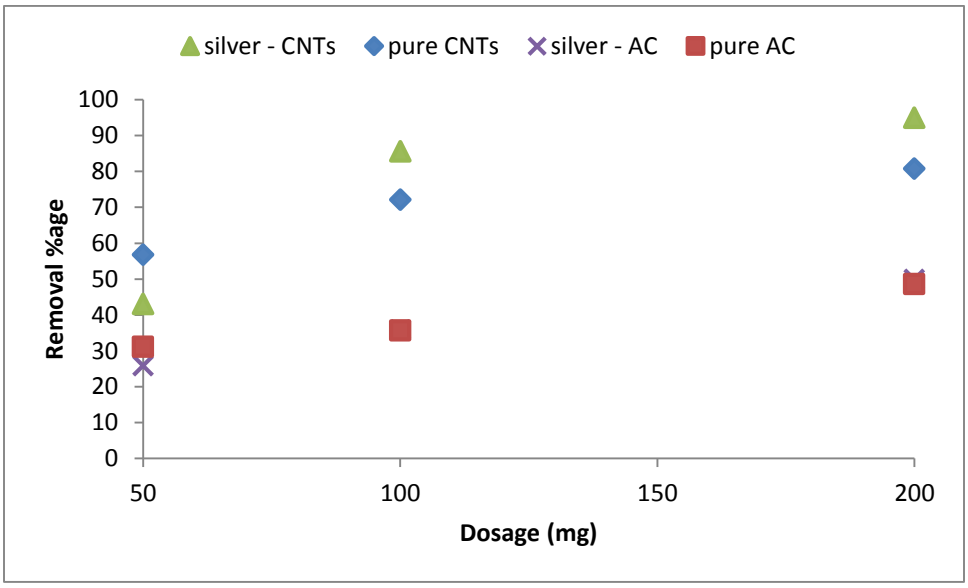

Figure 4.53 Effect of adsorbent dosage on percentage removal of arsenic using pure and silver impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, pH = 6)

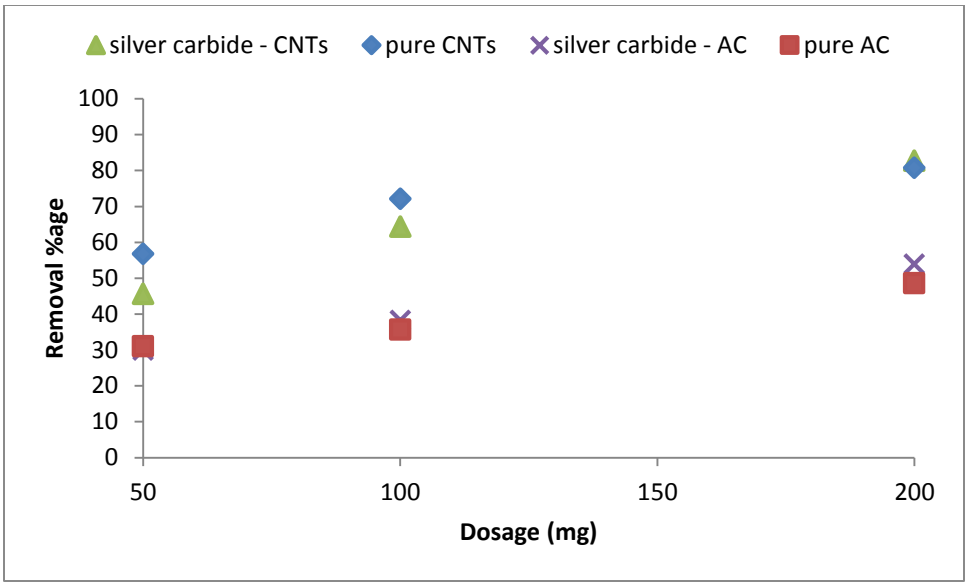

Figure 4.54 Effect of adsorbent dosage on percentage removal of arsenic using pure and silver carbide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, pH = 6)

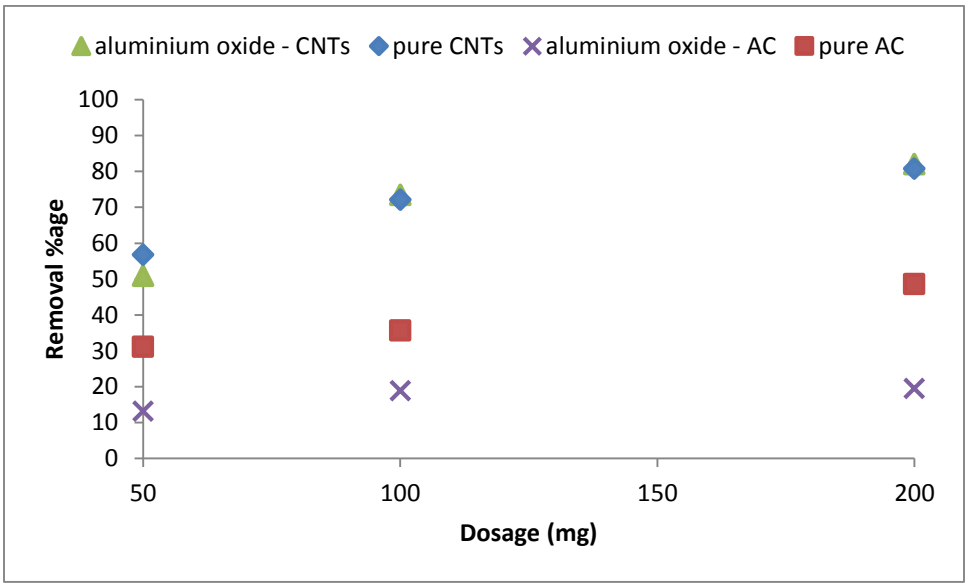

Figure 4.55 Effect of adsorbent dosage on percentage removal of arsenic using pure and aluminium oxide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, pH = 6)

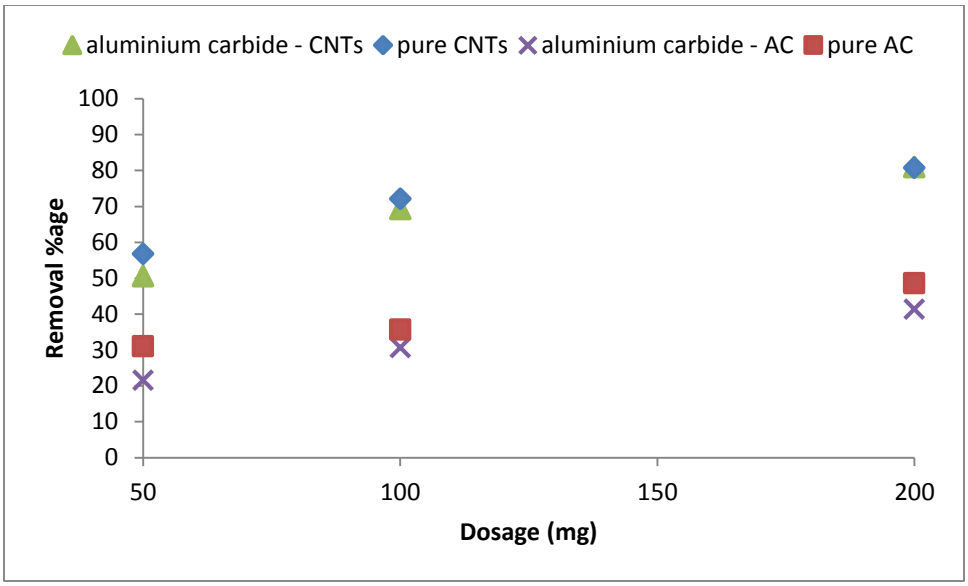

Figure 4.56 Effect of adsorbent dosage on percentage removal of arsenic using pure and aluminium carbide impregnated CNTs and AC (initial conc. = 1 ppm, contact time = 2 hrs, agitation speed = 200 rpm, pH = 6)

4.3.2.3 Effect of Contact Time (Agitation Time)

With an increase in agitation time, the adsorption of arsenic species increased with equilibrium approaching at about 4 to 5 hours of time.The equilibrium can be explained on the basis of the fact that with the passage of more and more time, the adsorption sites on the adsorbent are saturated and adsorption ceases at this point.The initial concentration of arsenic was kept constant at 1 ppm and it was seen that adsorption increased with time. The maximum removal (almost 100%) was achieved by iron oxide and aluminium oxide impregnated CNTs. This removal was obtained at 4 hours of time and it remained constant for another one hour to indicate the condition of equilibrium.

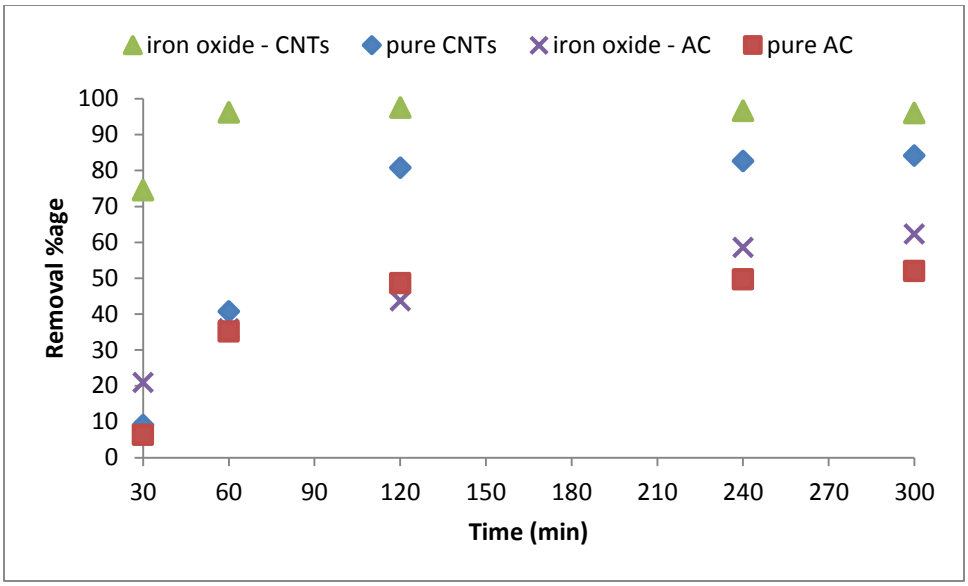

Figure 4.57 Effect of contact time on percentage removal of arsenic using pure and iron oxide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, agitation speed = 200 rpm, pH = 6)

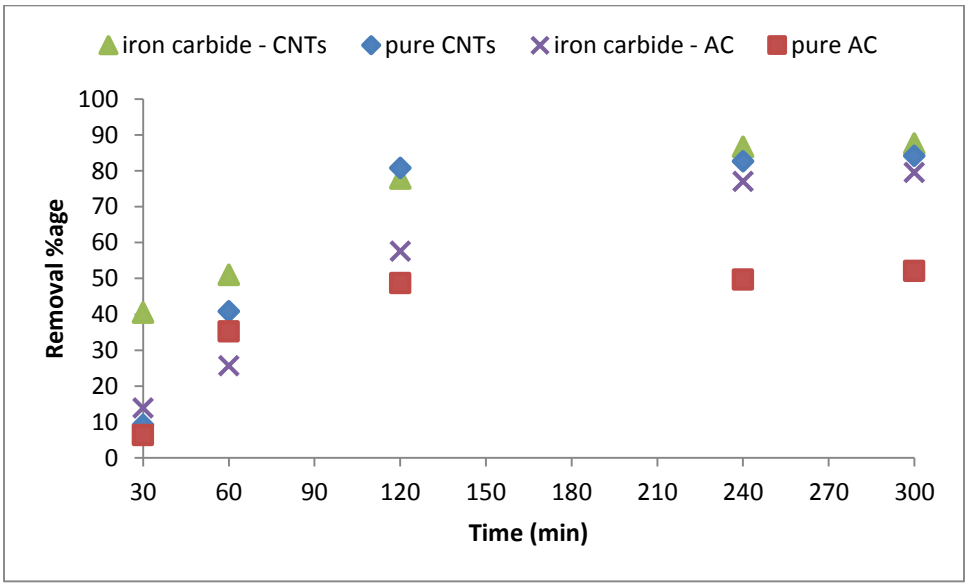

Figure 4.58 Effect of contact time on percentage removal of arsenic using pure and iron carbide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, agitation speed = 200 rpm, pH = 6)

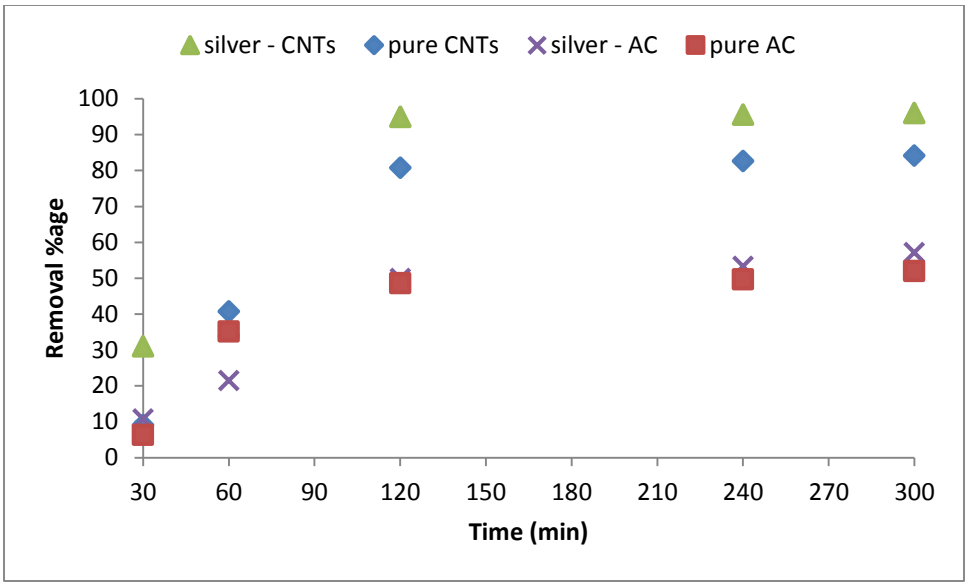

Figure 4.59 Effect of contact time on percentage removal of arsenic using pure and silver impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, agitation speed = 200 rpm, pH = 6)

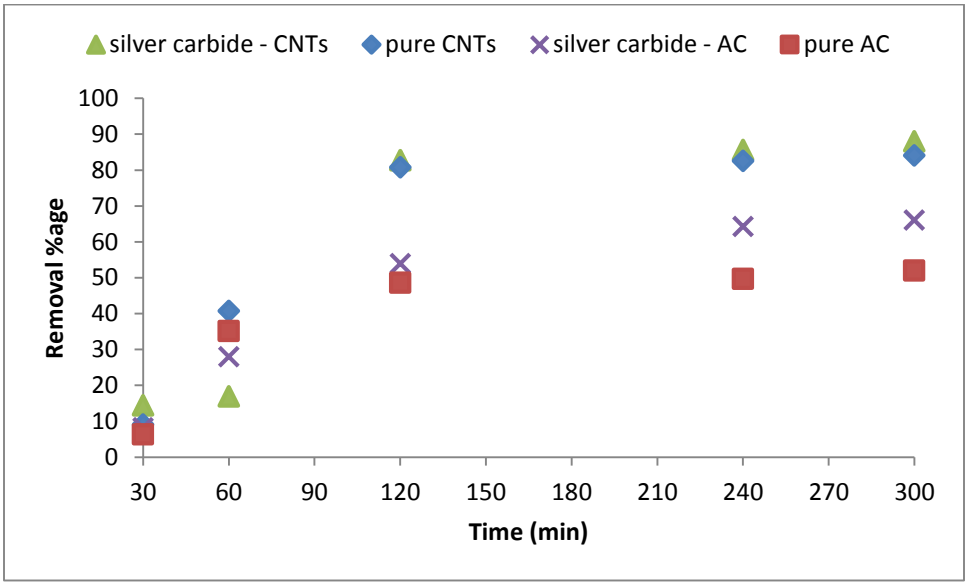

Figure 4.60 Effect of contact time on percentage removal of arsenic using pure and silver carbide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, agitation speed = 200 rpm, pH = 6)

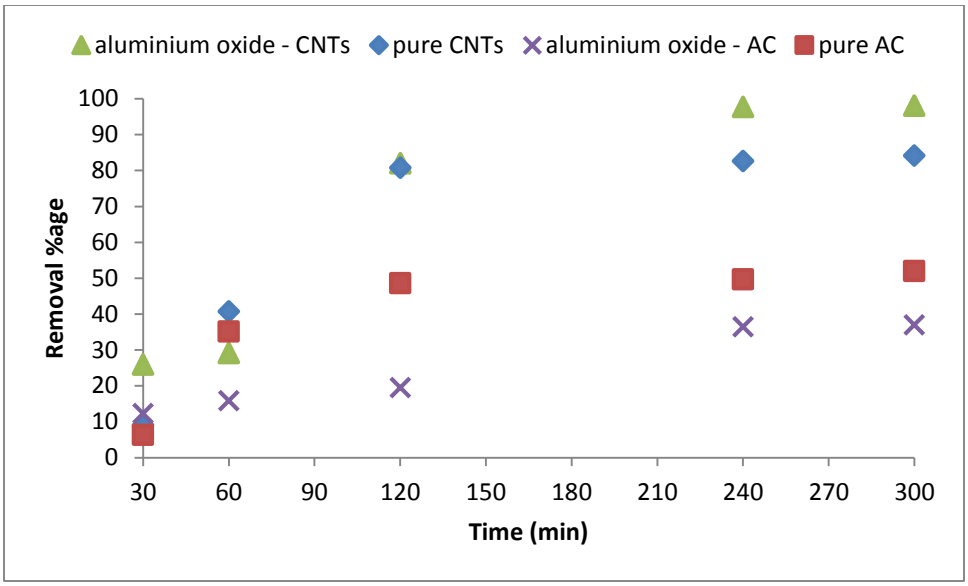

Figure 4.61 Effect of contact time on percentage removal of arsenic using pure and aluminium oxide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, agitation speed = 200 rpm, pH = 6)

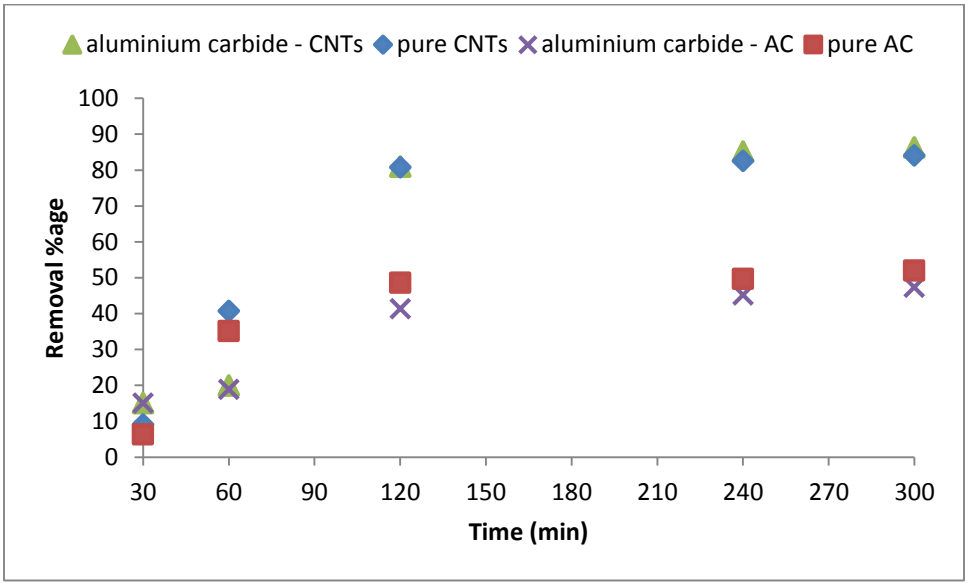

Figure 4.62 Effect of contact time on percentage removal of arsenic using pure and aluminium carbide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, agitation speed = 200 rpm, pH = 6)

4.3.2.4 Effect of Agitation Speed

Figures 4.63 to 4.68 represent results for effect of agitation speed on the removal of arsenic. With an increase in the diffusion of metal species towards the adsorbent with increasing speed, the adsorption has increased.External mass transfer effects are reduced to a great

extent [35]. This fast rate of mass transfer results in high adsorption and ultimately an increase in the removal of arsenic from water.

According to a study the removal of lead was enhanced from 33 to 39% by increasing the agitation speed from 50 to 150 rpm using carboxylic functionalized CNTs [56]. Sometimes the boundary layer of the adsorbent is reduced in thickness due to an increase in the agitation speed. It was observed that the removal of chromium (iron oxide - CNTs) was enhanced when the agitation speed was increased from 0 to 150 rpm [60].

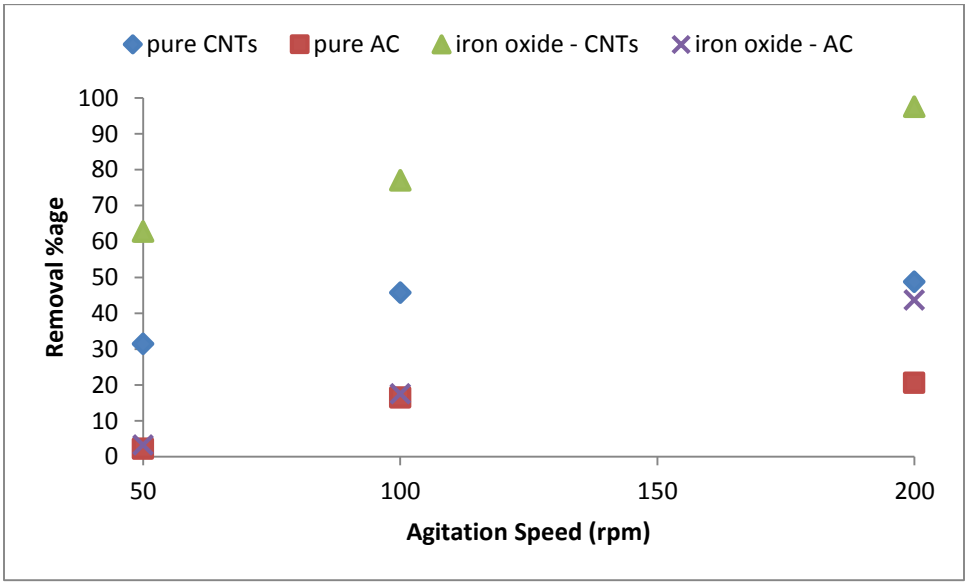

Figure 4.63 Effect of agitation speed on percentage removal of arsenic using pure and iron oxide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, contact time = 2 hrs, pH = 6)

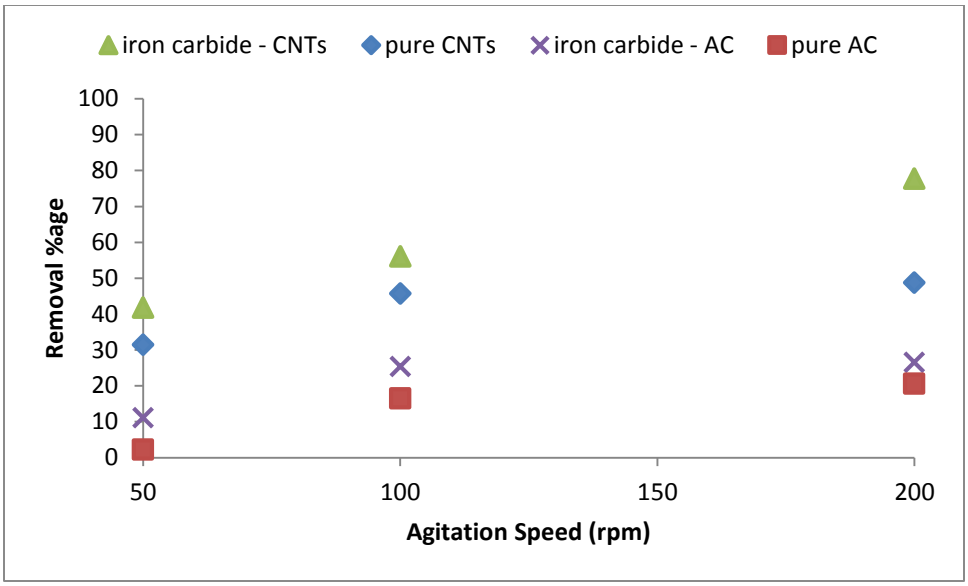

Figure 4.64 Effect of agitation speed on percentage removal of arsenic using pure and iron carbide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, contact time = 2 hrs, pH = 6)

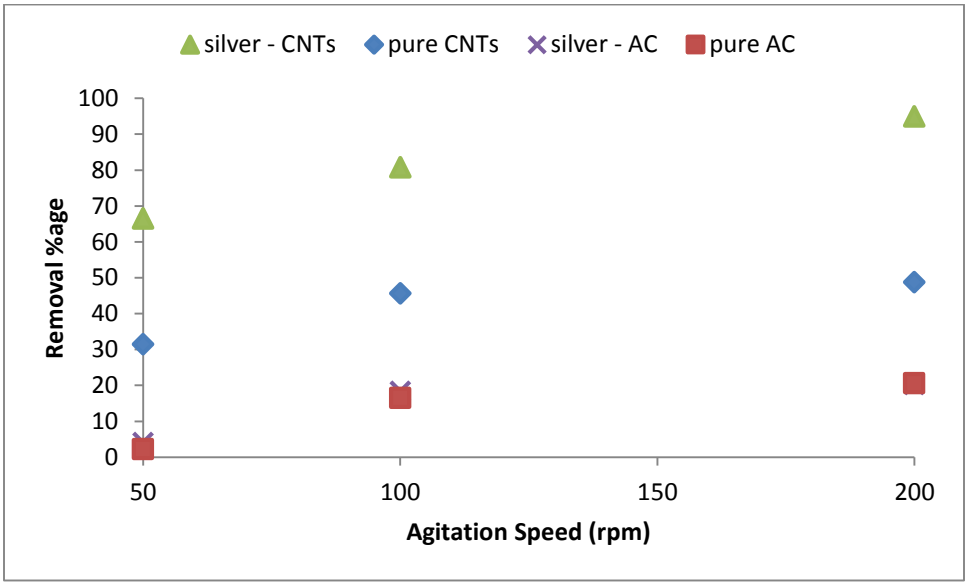

Figure 4.65 Effect of agitation speed on percentage removal of arsenic using pure and silver impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, contact time = 2 hrs, pH = 6)

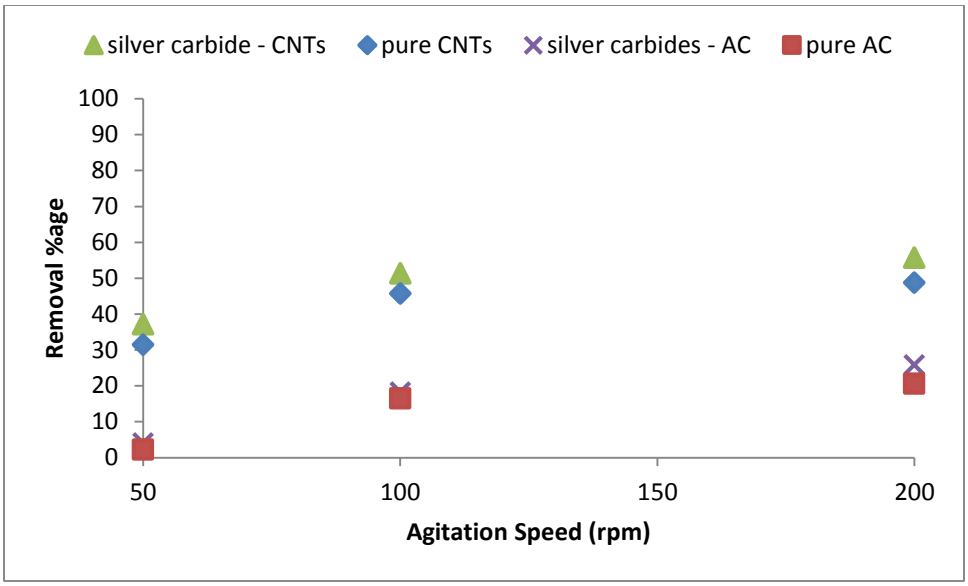

Figure 4.66 Effect of agitation speed on percentage removal of arsenic using pure and silver carbide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, contact time = 2 hrs, pH = 6)

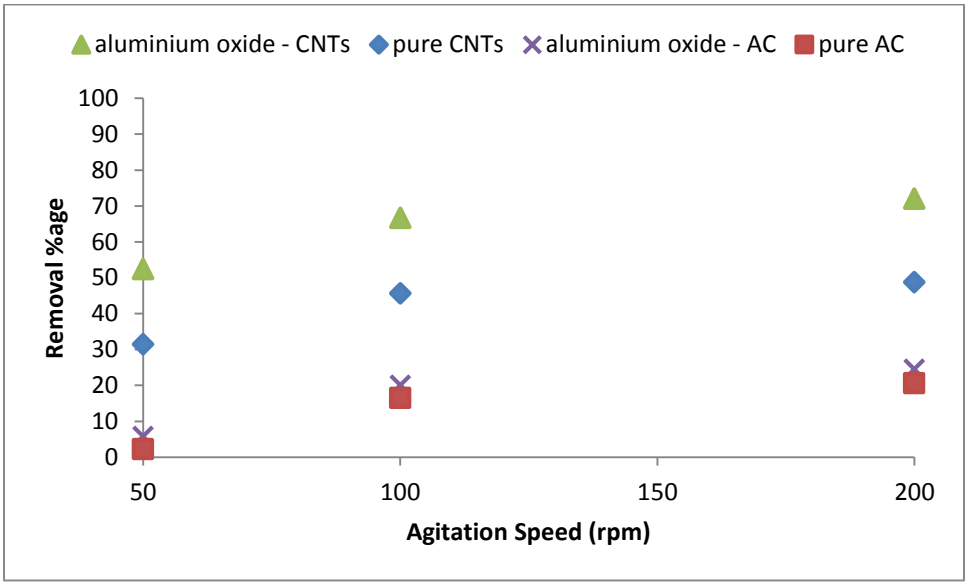

Figure 4.67 Effect of agitation speed on percentage removal of arsenic using pure and aluminium oxide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, contact time = 2 hrs, pH = 6)

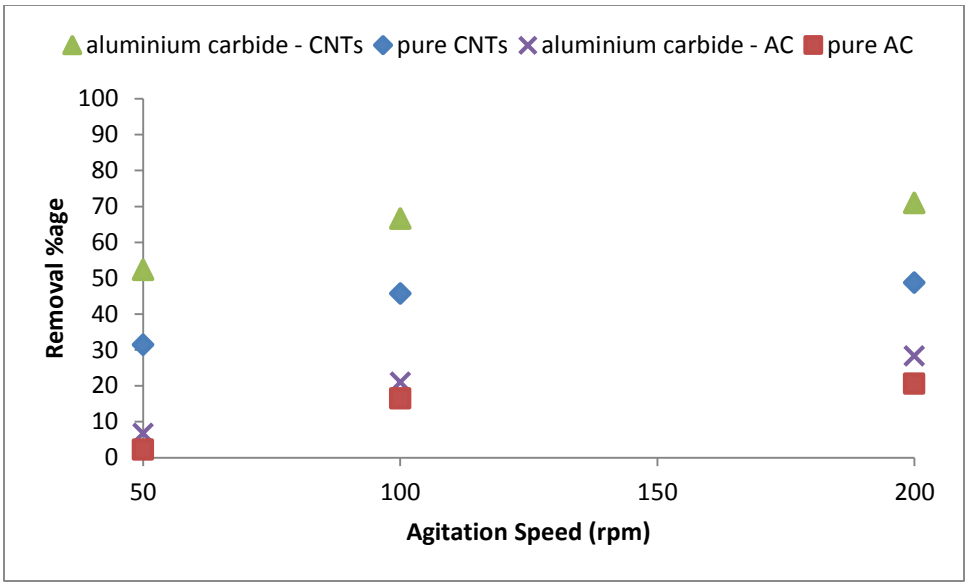

Figure 4.68 Effect of agitation speed on percentage removal of arsenic using pure and aluminium carbide impregnated CNTs and AC (initial conc. = 1 ppm, dosage = 200 mg, contact time = 2 hrs, pH = 6)

4.3.3. Removal of Lead (Pb^{2+}) Using Modified and Non Modified CNTs and AC

1 ppm of lead solution was subjected to modified and non-modified forms of AC and CNTs to find out the percentage removal of Pb from aqueous solution. The experimentations for lead were carried out at fixed parameters which were obtained as a result of optimization from the heavy metal removals of chromium and arsenic. The conditions for the experiment are as follows.

Conc. of initial solution	pH	Adsorbent dosage	Contact time	Agitation speed
1 ppm	6	200 mg	2 hrs	200 rpm

The results obtained for the removal of lead are summarized in Table 4.3.

Table 4.3 Percentage removal of lead with respect to different adsorbent materials

Adsorbent	Percentage Removal
Iron Oxide + CNT	99.144
Iron Oxide + AC	85.14
Iron Carbide + CNT	77.97
Iron Carbide + AC	59.6
Silver Oxide + CNT	61.17
Silver Oxide + AC	73.92
Silver Carbide + CNT	8.5
Silver Carbide + AC	22.18
Aluminium Oxide + CNT	23.87
Aluminium Oxide + AC	30.56
Aluminium Carbide + CNT	25.28
Aluminium Carbide + AC	4.49
Pure AC	37.33
Pure CNT	20.21

In this set of experiment, the initial solution was prepared with the help of a buffer solution of pH=6 in order to prevent the precipitation of lead ions at the required pH value. Normally, with the variation of pH, there is possibility that lead will precipitate out which

greatly affects the concentration analysis after the experiment. In the case when functionalized CNTs were used for the removal of lead from water, the best results were obtained at pH 7. At lower pH, the protonation prevents removal. On pH exceeding 7, precipitation of lead occurs which is why a constant pH is a must to observe removal results [56]

Moreover, we can observe that the iron impregnated adsorbents have given the highest removal of lead ions. These results are much better than the ones for functionalized CNTs which give a mere 39% removal at pH 6 as compared to the present results of iron impregnated CNTs which are 99%.

4.4. Freundlich and Langmuir Isotherms Models

Langmuir and Fruendlich isotherms are graphs drawn at constant temperature which describe the relation between adsorption of molecular species onto the adsorbent surface and the concentration of the medium which contains the adsorbent. For this work, the experimental data of removal of chromium and arsenic has been fitted with the Langmuir and Fruendlich isotherm models. In this way the adsorption of these metal species onto the surface of our carbon adsorbents can be estimated.

4.4.1. Langmuir and Freundlich Adsorption Isotherm Models for Chromium

Figures 4.69 to 4.72 represent the Langmuir isotherm models for chromium whereas Figures 4.73 to 4.76 represent the Fruendlich isotherm models for chromium. Each isotherm depicts its correlation coefficient (the value of R^2). The experimental equilibrium data is found to have a good fit with the Langmuir adsorption isotherms in the case of most adsorbents. For example, Figure 4.70 (a) has a value of R^2 equals to 0.9966. This is the case of iron impregnated CNTs as the adsorbent. On the other hand we have adsorbents

like silver – AC and silver carbide – AC which have very low values of R^2 (0.5731 and 0.1805 respectively). But in the case of these adsorbents, we find a very good fit with Fruendlich isotherms where the same adsorbents have R^2 values of 0.7955 and 0.9949 respectively. With the present results, it can be inferred that in the case of chromium we have monolayer adsorption where only the surface of material is being used for the adsorption. The good fitting of data that we see in the Figures depicts the fact that chromium ions have strong linkage of adsorption with the impregnated adsorbents. Table4.4 represents the parameters from the Langmuir and Fruendlich isotherms.

Langmuir and Fruendlich isotherm models have been used a number of times to determine the adsorption of various heavy metals onto carbon adsorbents. Carboxylic functionalized CNTs have been used to remove lead from water and the adsorption is found to follow monolayer adsorption with values of R^2 being 0.9731 and 0.9971 respectively [56]. Similarly, trivalent was removed from water using carboxylic modified CNTs and the R^2 values obtained for Langmuir and Fruendlich were 0.9089 and 0.9494. The value of q_m for these modified was 0.3853 whereas in our work the highest value of q_m is given by aluminium carbide impregnated CNTs (1.30253) [35].

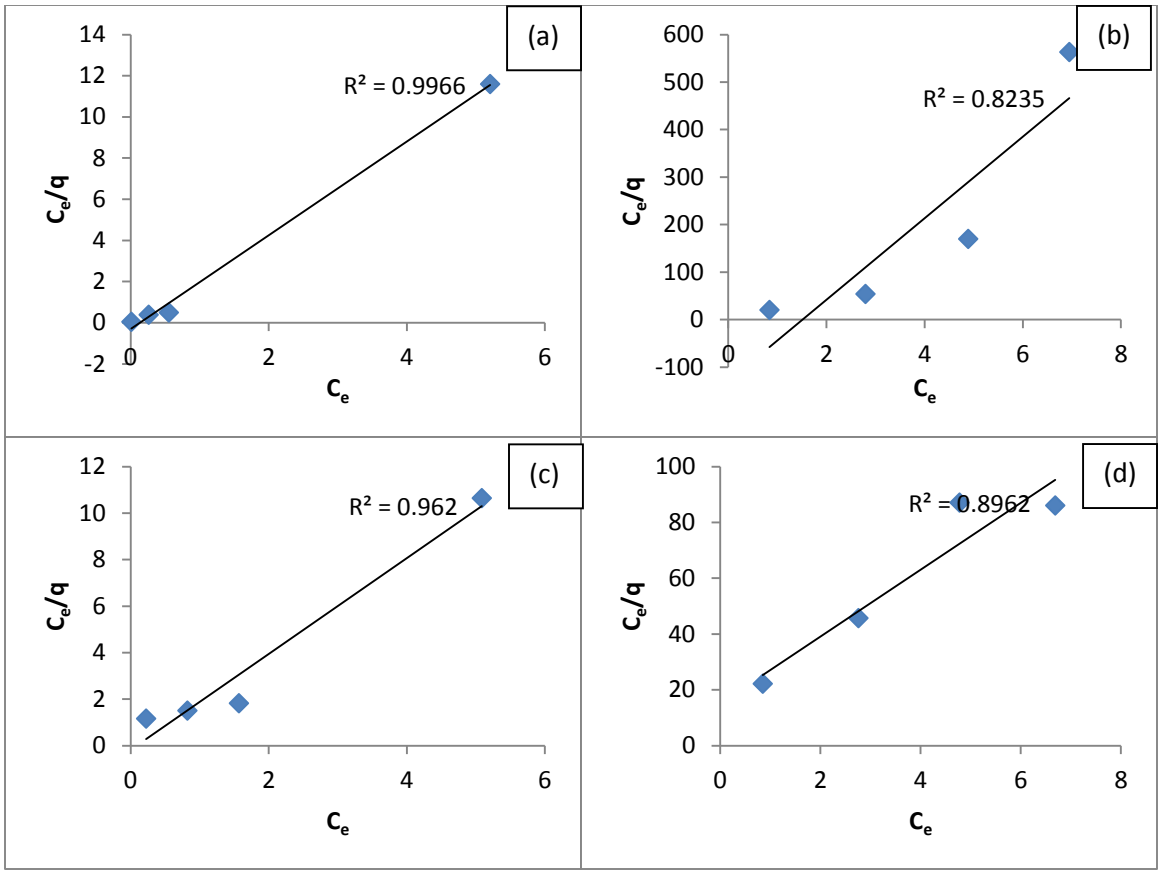

Figure 4.69 Langmuir isotherms for adsorption of chromium on iron impregnated CNTs and AC (a) iron oxide – CNTs (b) iron oxide – AC (c) iron carbide – CNTs (d) iron carbide - AC

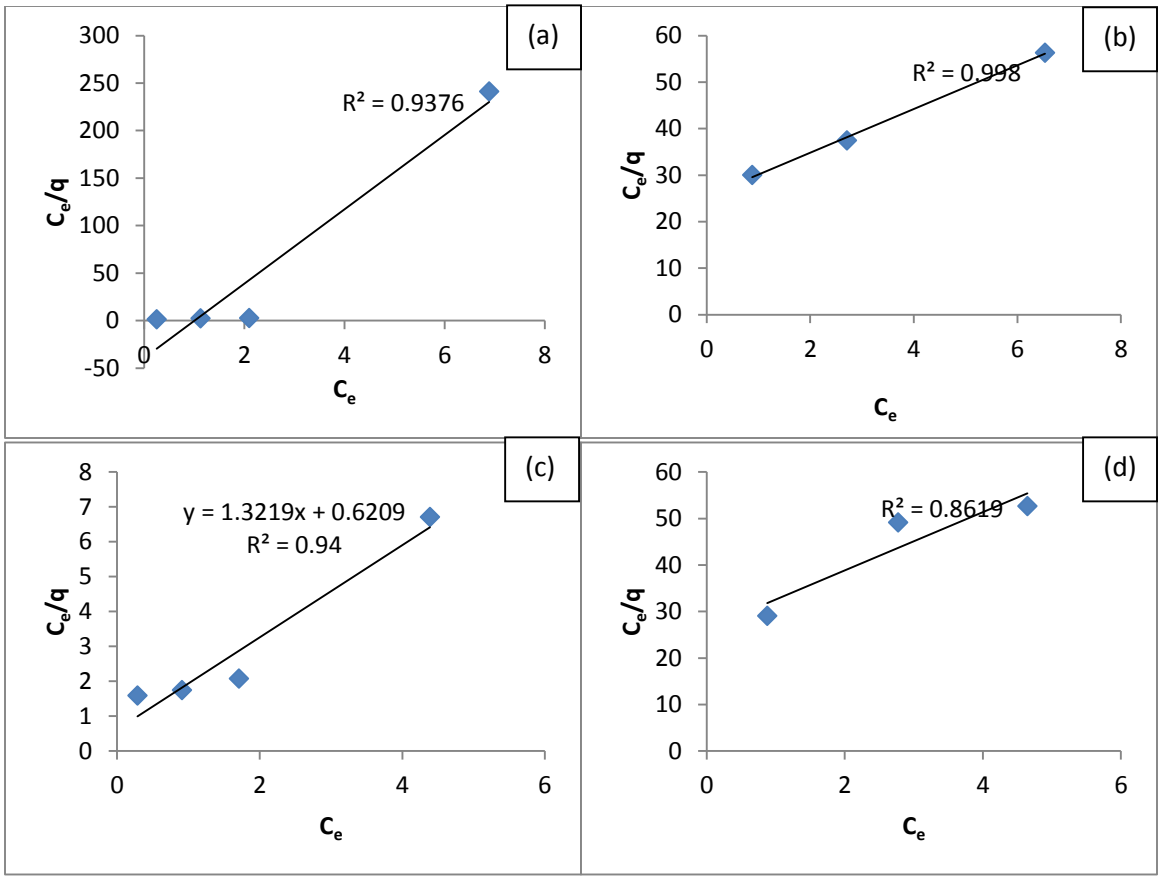

Figure 4.70 Langmuir isotherms for adsorption of chromium on silver impregnated CNTs and AC (a) silver – CNTs (b) silver – AC (c) silver carbide – CNTs (d) silver carbide - AC

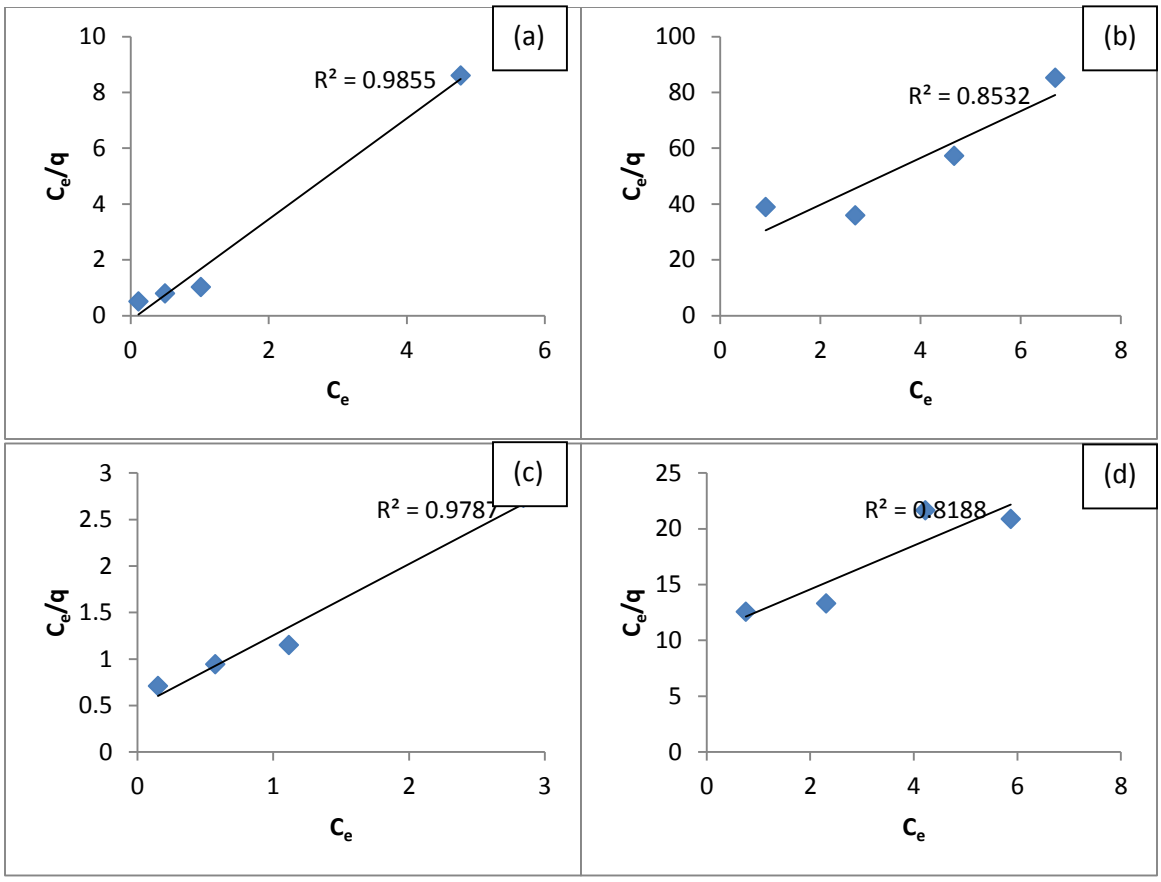

Figure 4.71 Langmuir isotherms for adsorption of chromium on aluminium impregnated CNTs and AC (a) aluminium oxide – CNTs (b) aluminium oxide – AC (c) aluminium carbide – CNTs (d) aluminium carbide - AC

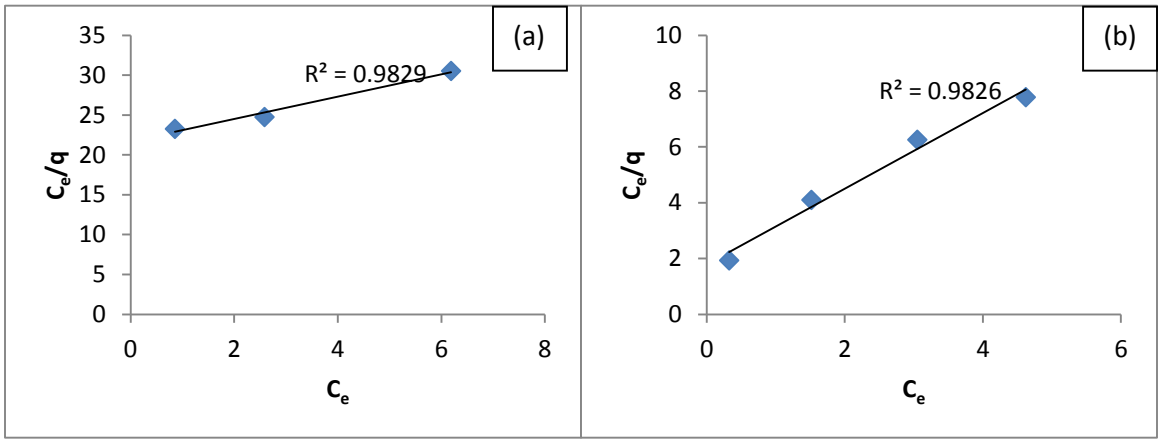

Figure 4.72 Langmuir isotherms for adsorption of chromium on pure CNTs and AC (a) Pure AC (b) Pure CNTs

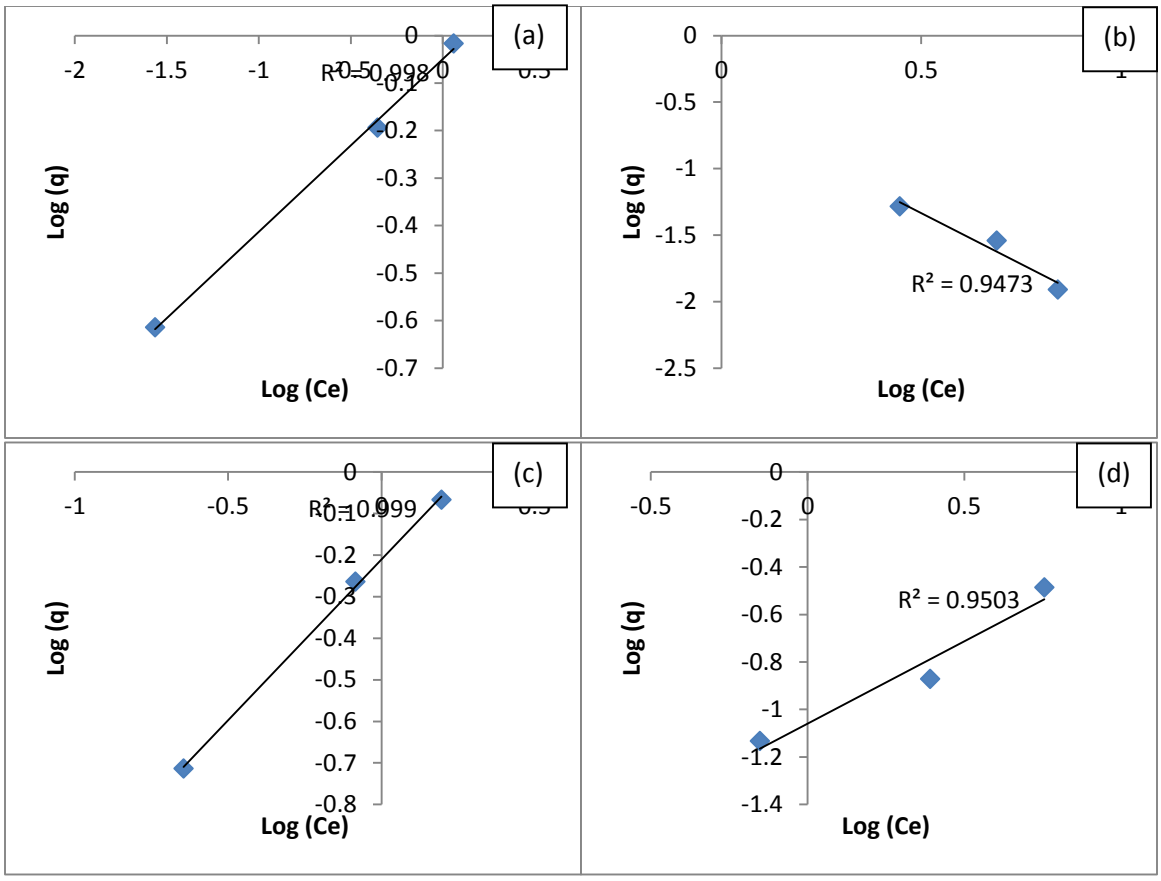

Figure 4.73 Fruendlich isotherms for adsorption of chromium on iron impregnated CNTs and AC (a) iron oxide – CNTs (b) iron oxide – AC (c) iron carbide – CNTs (d) iron carbide - AC

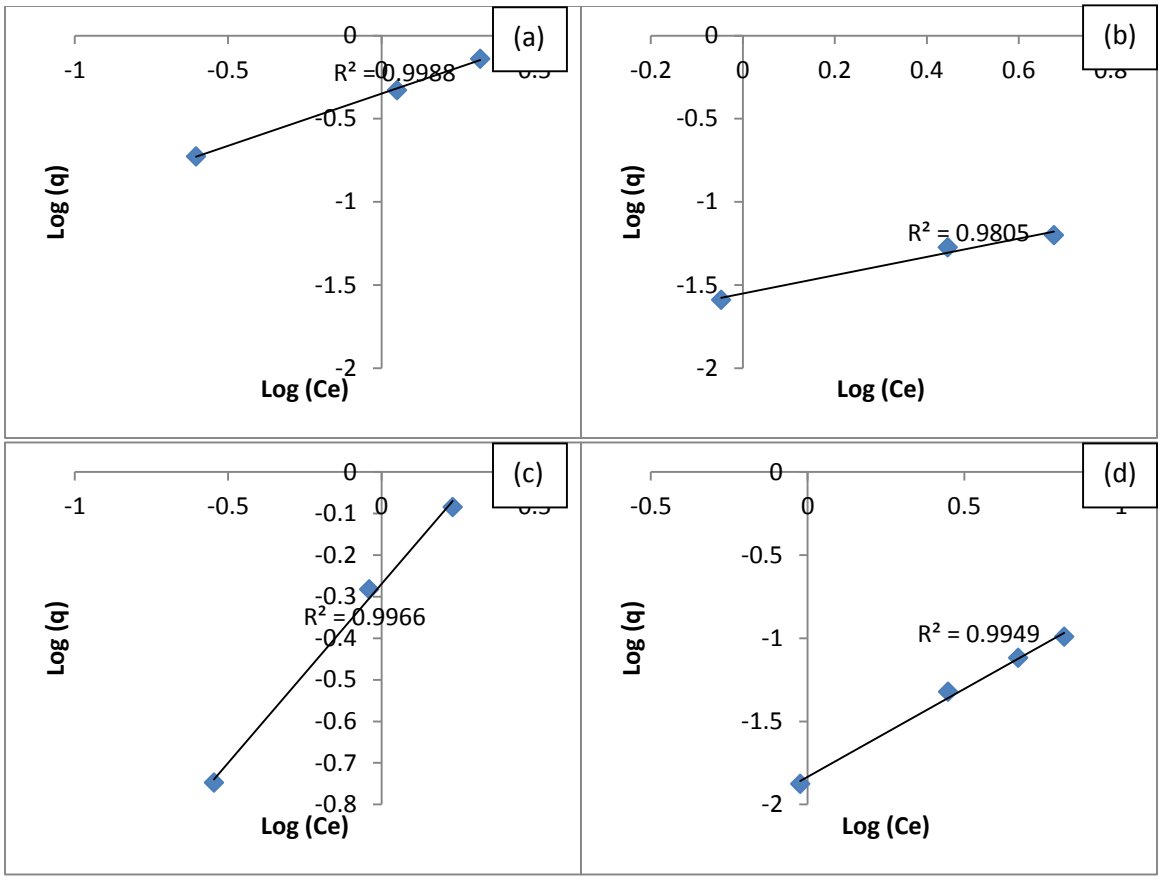

Figure 4.74 Fruendlich isotherms for adsorption of chromium on silver impregnated CNTs and AC (a) silver – CNTs (b) silver – AC (c) silver carbide – CNTs (d) silver carbide - AC

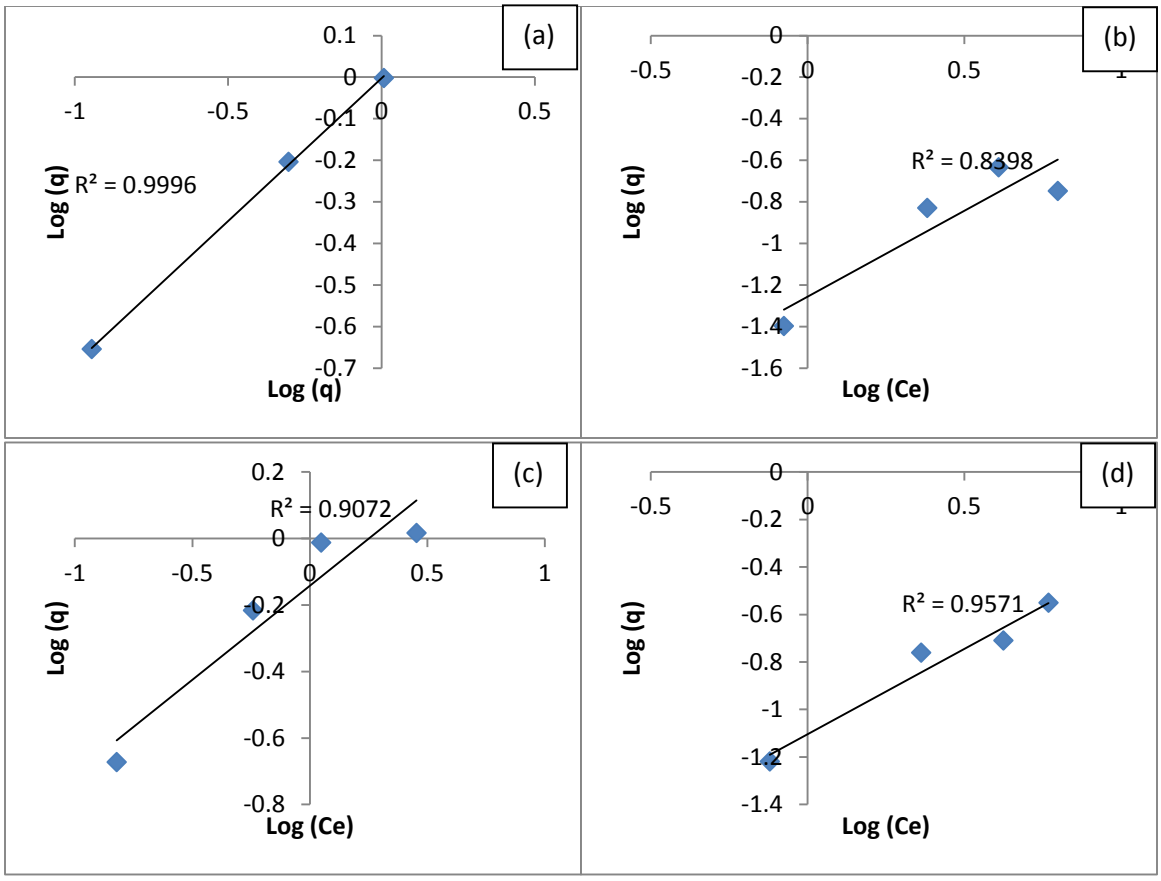

Figure 4.75 Fruendlich isotherms for adsorption of chromium on aluminium impregnated CNTs and AC (a) aluminium oxide – CNTs (b) aluminium oxide – AC (c) aluminium carbide – CNTs (d) aluminium carbide - AC

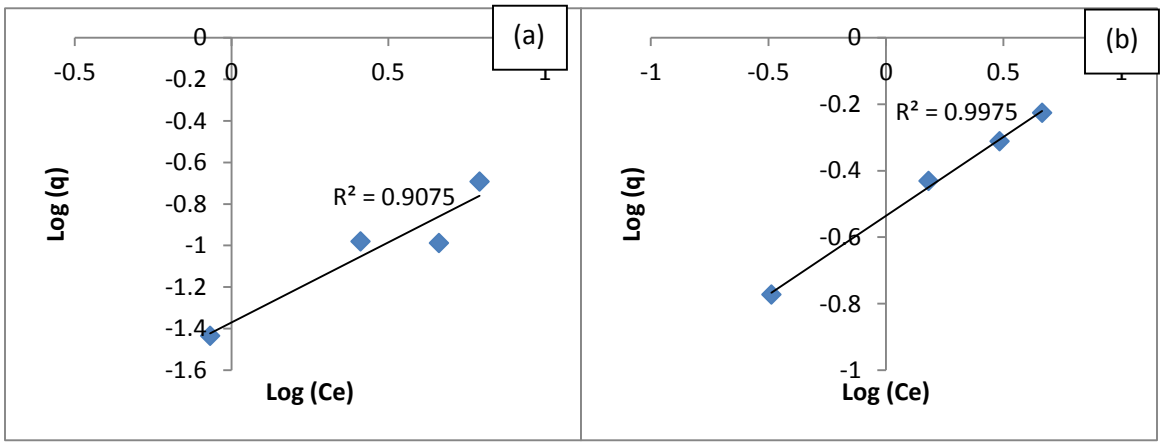

Figure 4.76 Fruendlich isotherms for adsorption of chromium on pure CNTs and AC (a) Pure AC (b) Pure CNTs

Table 4.4 Parameters of Langmuir and Fruendlich isotherm models for chromium

Adsorbent	Fruendlich		Langmuir	
	n	K_F (L/mg)	q_m (mg/g)	K_L (L/mg)
Iron Oxide + CNT	7.922564	0.628705	0.438981	-7.47535
Iron Oxide + AC	-43.2964	0.029277	0.028802	3.024642
Iron Carbide + CNT	3.158457	0.441889	0.485144	-11.2708
Iron Carbide + AC	1.726007	0.084618	0.408657	0.221736
Silver Oxide + CNT	-2.1562	0.242919	0.025581	-0.99706
Silver Oxide + AC	1.155086	0.025193	0.730199	0.031365
Silver Carbide + CNT	1.988141	0.435627	0.756463	2.128985
Silver Carbide + AC	0.944618	0.014662	-1.12067	-0.01323
Aluminium Oxide + CNT	3.907029	0.571687	0.552656	-10.9559
Aluminium Oxide + AC	1.212097	0.055528	0.375455	0.198548
Aluminium Carbide + CNT	1.76825	0.721239	1.302523	1.580719
Aluminium Carbide + AC	1.392318	0.078633	0.510843	0.183569
Pure AC	1.299802	0.042645	0.407319	0.111203
Pure CNT	2.110755	0.291322	0.737584	0.756502

4.4.2. Langmuir and Freundlich Adsorption Isotherm Models for Arsenic

Figures 4.77 to 4.81 represent the Langmuir isotherm models for arsenic whereas Figures 4.82 to 4.85 represent the Fruendlich isotherm models for arsenic. R^2 for each plot indicate a good fit with Langmuir adsorption. For instance, Figure 4.77 (a) has a value of R^2 equals to 0.9893. This is the case of iron impregnated CNTs as the adsorbent. The data is also found to be in good fit the Fruendlich isotherms. We can see a very high value of R^2 for the silver – AC adsorbent in Figure 4.83 (d)(i.e. 0.9949). With the present results, it can be inferred that in the case of arsenic we have monolayer adsorption where only the surface of material is being used for the adsorption. The good fitting of data that we see in the Figures depicts the fact that arsenic ions have strong linkage of adsorption with the impregnated adsorbents.

Table 4.5 represents the parameters from the Langmuir and Fruendlich isotherms.

Langmuir and Fruendlich isotherm models have been used a number of times to determine the adsorption of various heavy metals onto carbon adsorbents. The adsorption of hexavalent chromium on acid modified AC and CNTs was studied using the Langmuir and Fruendlich isotherms and the R^2 values calculated were 0.940 and 0.918 respectively [59].

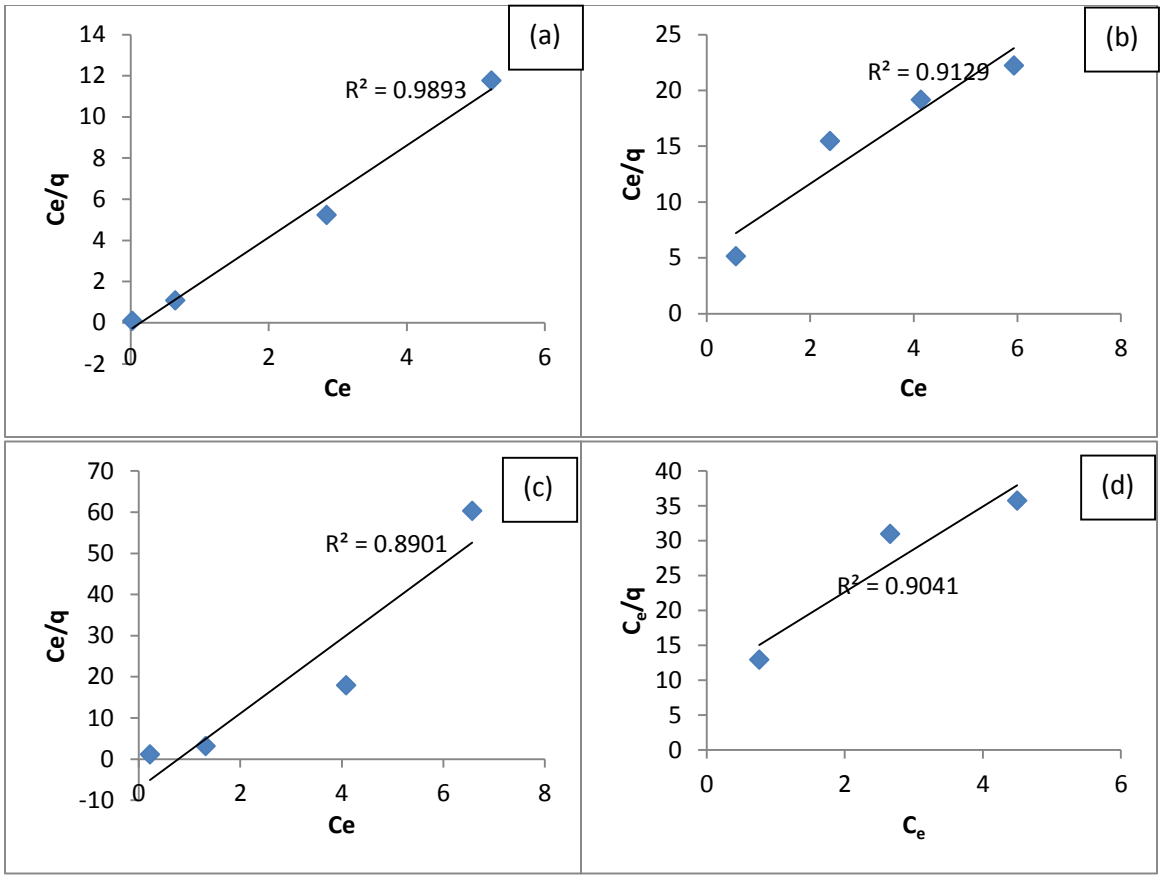

Figure 4.77 Langmuir isotherms for adsorption of arsenic on iron impregnated CNTs and AC (a) iron oxide – CNTs (b) iron oxide – AC (c) iron carbide – CNTs (d) iron carbide - AC

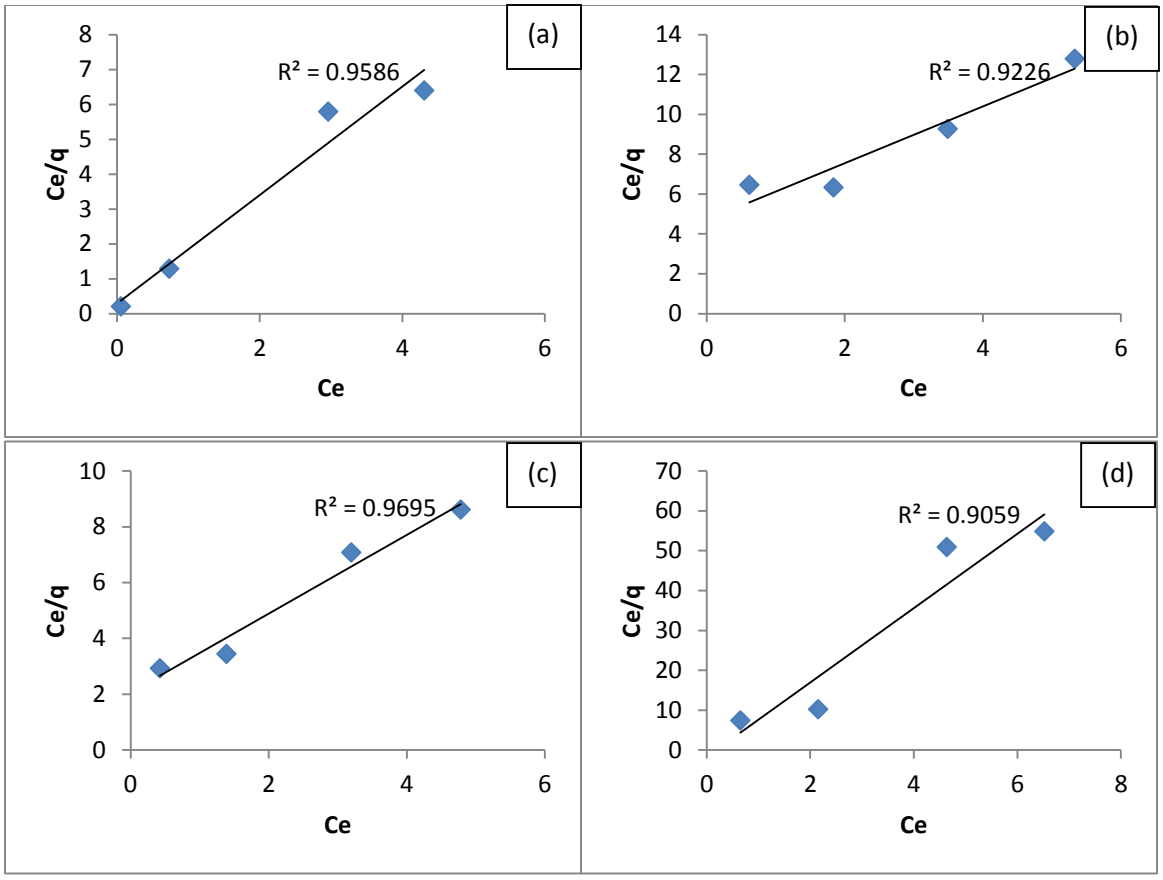

Figure 4.78 Langmuir isotherms for adsorption of arsenic on silver impregnated CNTs and AC (a) silver – CNTs (b) silver – AC (c) silver carbide – CNTs (d) silver carbide - AC

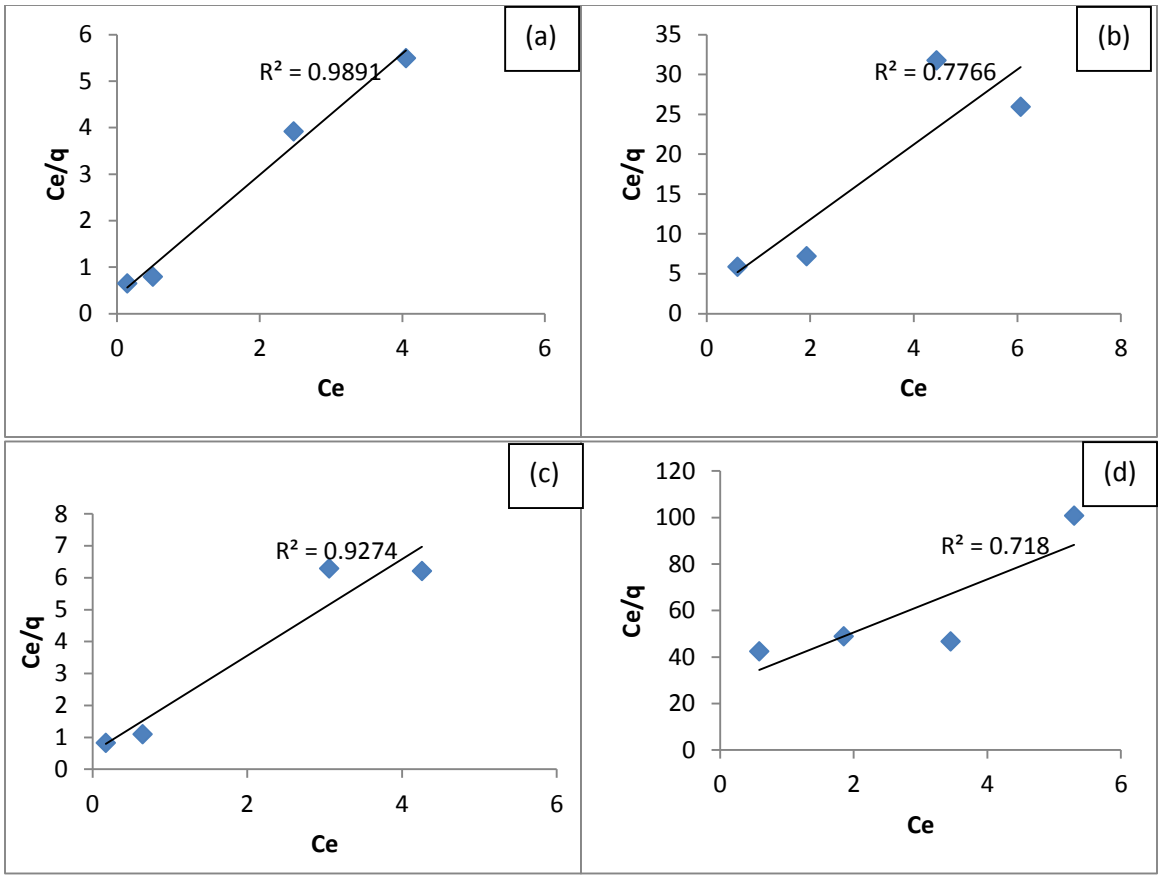

Figure 4.79 Langmuir isotherms for adsorption of arsenic on aluminium impregnated CNTs and AC (a) aluminium oxide – CNTs (b) aluminium oxide – AC (c) aluminium carbide – CNTs (d) aluminium carbide - AC

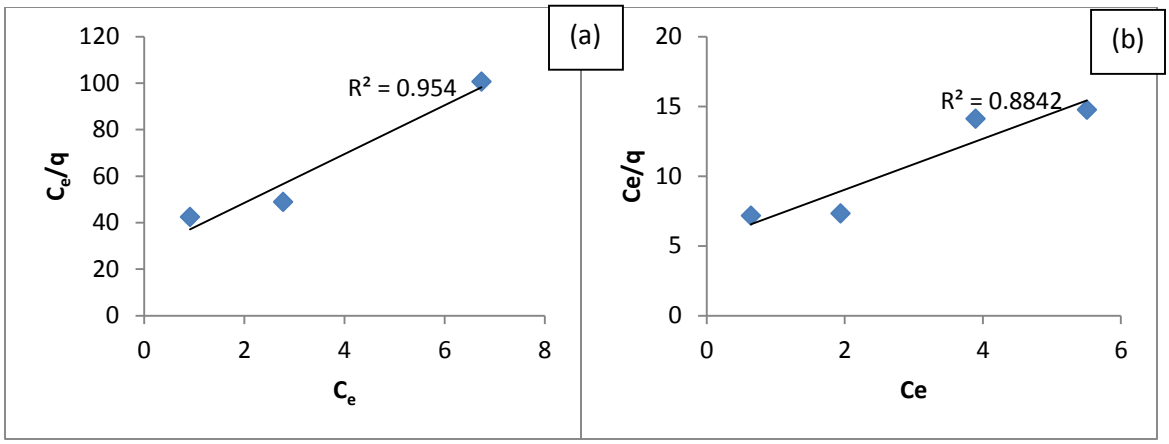

Figure 4.80 Langmuir isotherms for adsorption of arsenic on pure CNTs and AC (a) Pure AC (b) Pure CNTs

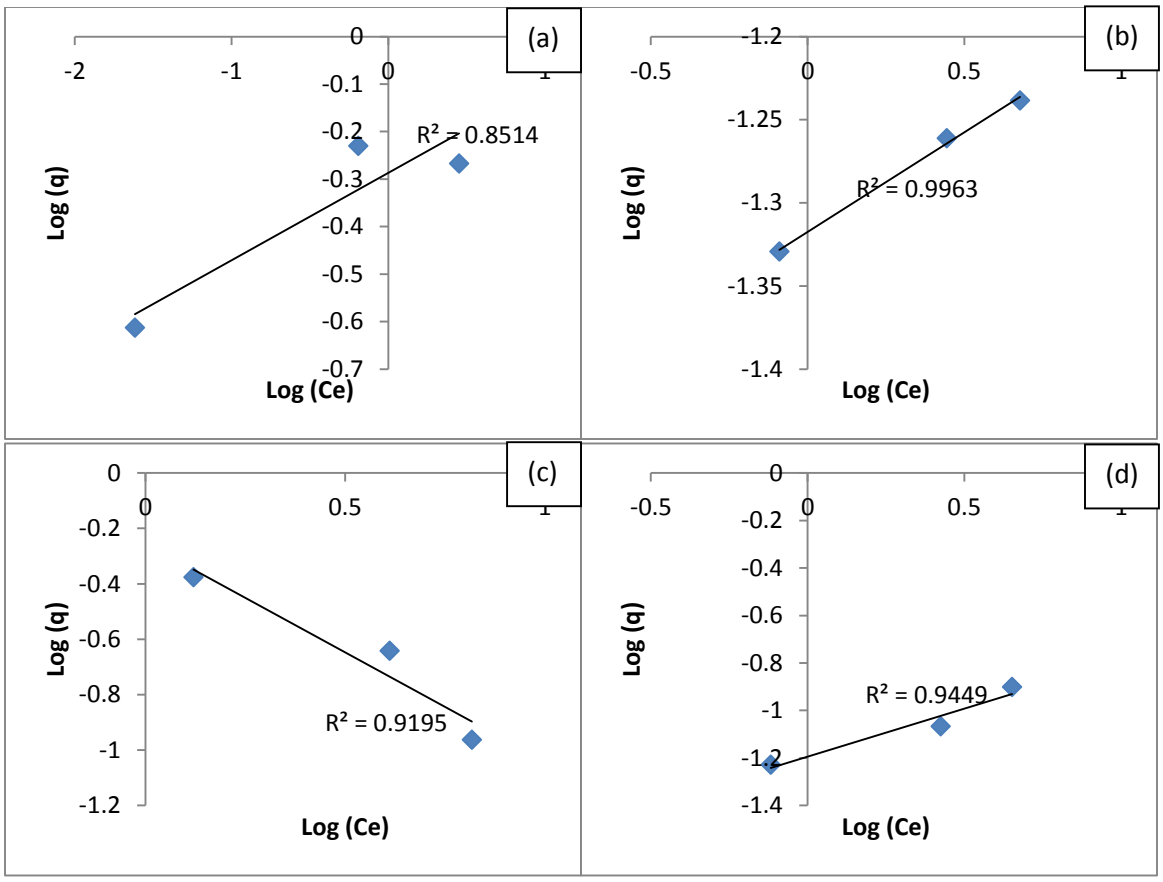

Figure 4.81 Fruendlich isotherms for adsorption of arsenic on iron impregnated CNTs and AC (a) iron oxide – CNTs (b) iron oxide – AC (c) iron carbide – CNTs (d) iron carbide - AC

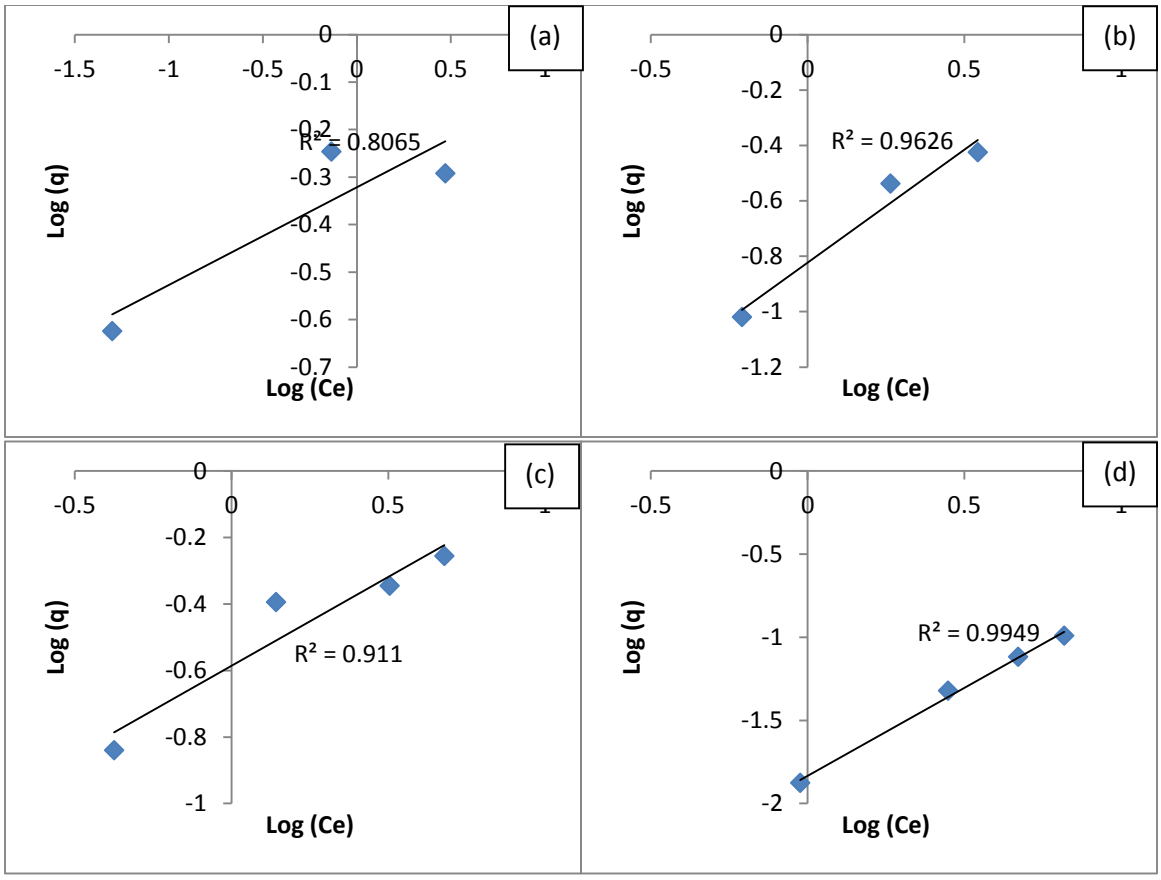

Figure 4.82 Fruendlich isotherms for adsorption of arsenic on silver impregnated CNTs and AC (a) silver – CNTs (b) silver – AC (c) silver carbide – CNTs (d) silver carbide - AC

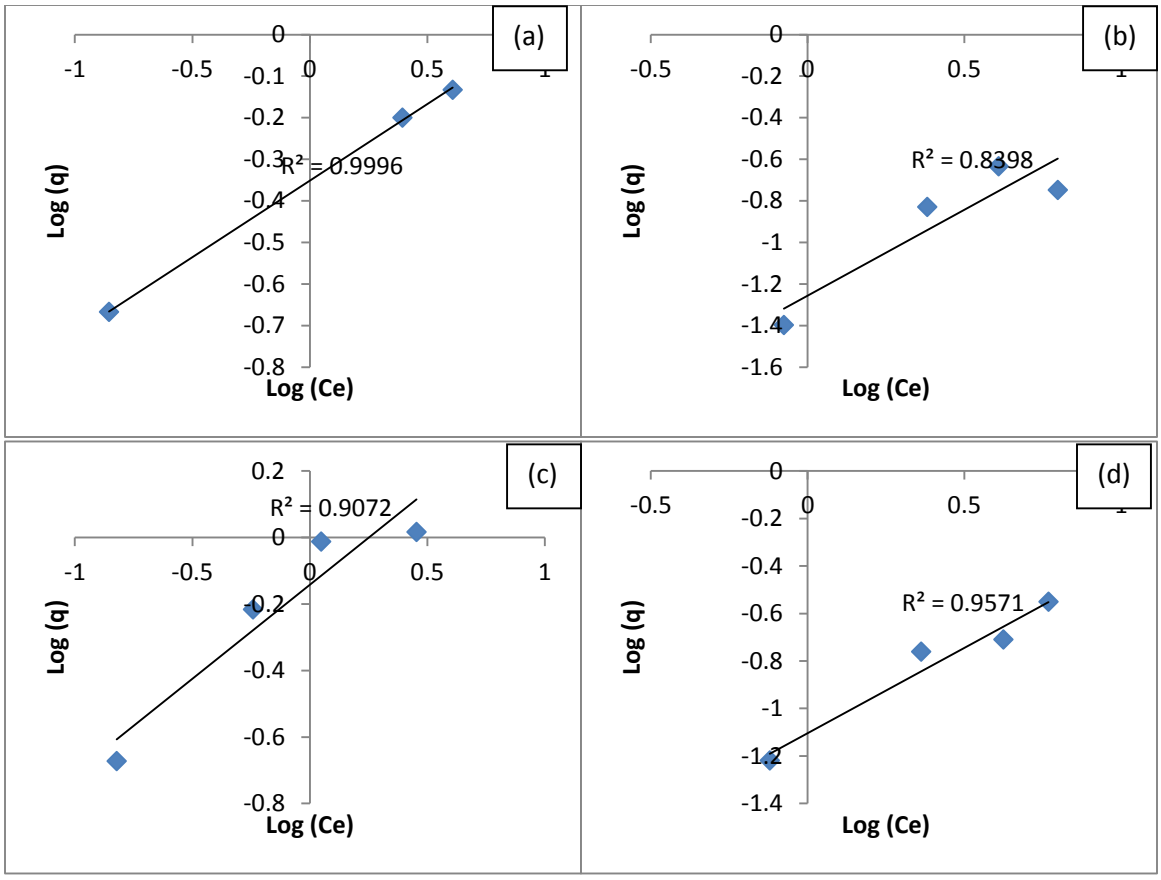

Figure 4.83 Fruendlich isotherms for adsorption of arsenic on aluminium impregnated CNTs and AC (a) aluminium oxide – CNTs (b) aluminium oxide – AC (c) aluminium carbide – CNTs (d) aluminium carbide - AC

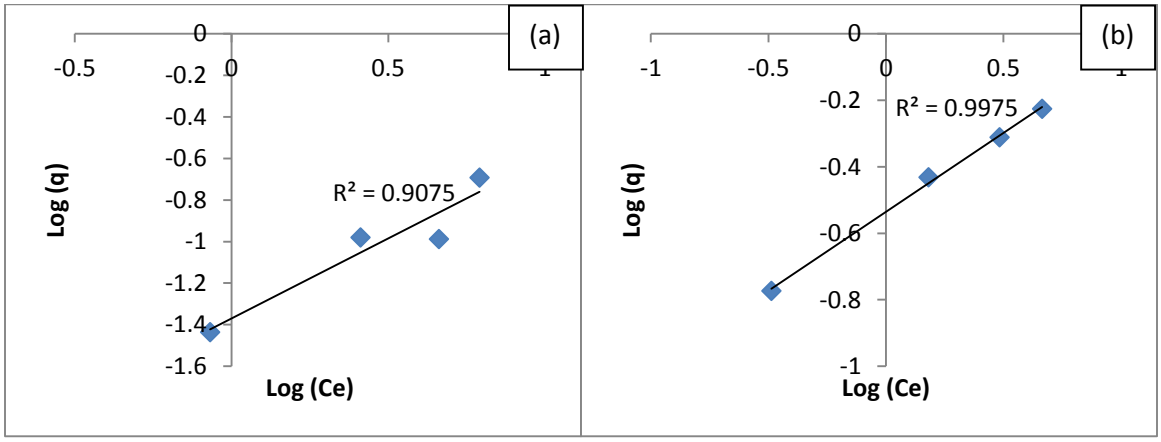

Figure 4.84 Fruendlich isotherms for adsorption of arsenic on pure CNTs and AC (a) Pure AC (b) Pure CNTs

Table 4.5 Parameters of Langmuir and Fruendlich isotherm models for arsenic

Adsorbent	n	K_F (L/mg)	q_m (mg/g)	K_L (L/mg)
Iron Oxide + CNT	7.922564	0.628705	0.447496	-6.85718
Iron Oxide + AC	-43.2964	0.029277	0.324378	0.562603
Iron Carbide + CNT	3.158457	0.441889	0.109998	-1.28279
Iron Carbide + AC	1.726007	0.084618	0.051781	-1.13223
Silver Oxide + CNT	-2.1562	0.242919	0.643574	5.227921
Silver Oxide + AC	1.155086	0.025193	0.701529	0.30373
Silver Carbide + CNT	1.988141	0.435627	0.708868	0.683536
Silver Carbide + AC	0.944618	0.014662	0.107277	-5.50091
Aluminium Oxide + CNT	3.907029	0.571687	0.767279	3.420155
Aluminium Oxide + AC	1.212097	0.055528	0.212684	1.968024
Aluminium Carbide + CNT	1.76825	0.721239	0.661965	2.827743
Aluminium Carbide + AC	1.392318	0.078633	0.676466	0.348777
RAW AC	1.299802	0.042645	0.10908	0.363366
RAW CNT	2.110755	0.291322	0.54802	0.339335

4.5. Kinetic Adsorption Modeling

The pseudo second order model was used to model the kinetics of adsorption. The R^2 values for all adsorbents were found to be nearing unity. This explains the fact that pseudo second order model can be used to study the mechanism of adsorption of both, chromium and arsenic with CNTs and AC as adsorbents. The following Figures represent the fitting of

experimental data with the pseudo second order model. These plots were created using the data obtained for adsorption experiments conducted at five different time intervals.

4.5.1. Kinetic Adsorption Modeling for Chromium with CNTs and AC as Adsorbents

The adsorption kinetics was studied at a pH of 6. The parameters of modeling have been tabulated in Table 4.6. The correlation coefficient of each plot is mentioned along each straight line plot.

Similarly, three different types of activated carbon prepared from agricultural wastes were used for adsorption of hexavalent chromium from aqueous solution and the kinetics were studied using pseudo second order and pseudo first order models. The R^2 values found were of the order of 0.99 [77].

In one such work, hexavalent chromium was removed with the help of acid modified CNTs and AC. The adsorption kinetic model which was most suitable in this case was also the pseudo second order model which gave R^2 values of 0.999 for all adsorbents apart from the modified AC which was 0.994. The values of q_e and k_2 for modified CNTs were 0.964 and 0.059 respectively and 2.024 and 0.011 for AC respectively [59].

Similarly in another related research, carboxylic group was attached onto the surface of CNTs and trivalent chromium was adsorbed onto it. The kinetics followed the pseudo second order model with high values of R^2. The value of adsorption capacity of modified CNTs at equilibrium (q_e) was found to be 0.5 in this case [35]. The value of q_e for iron oxide and aluminium oxide impregnated CNTs were found to be around 0.25. The reason for a low value is the low initial concentration (1 ppm) used in our work.

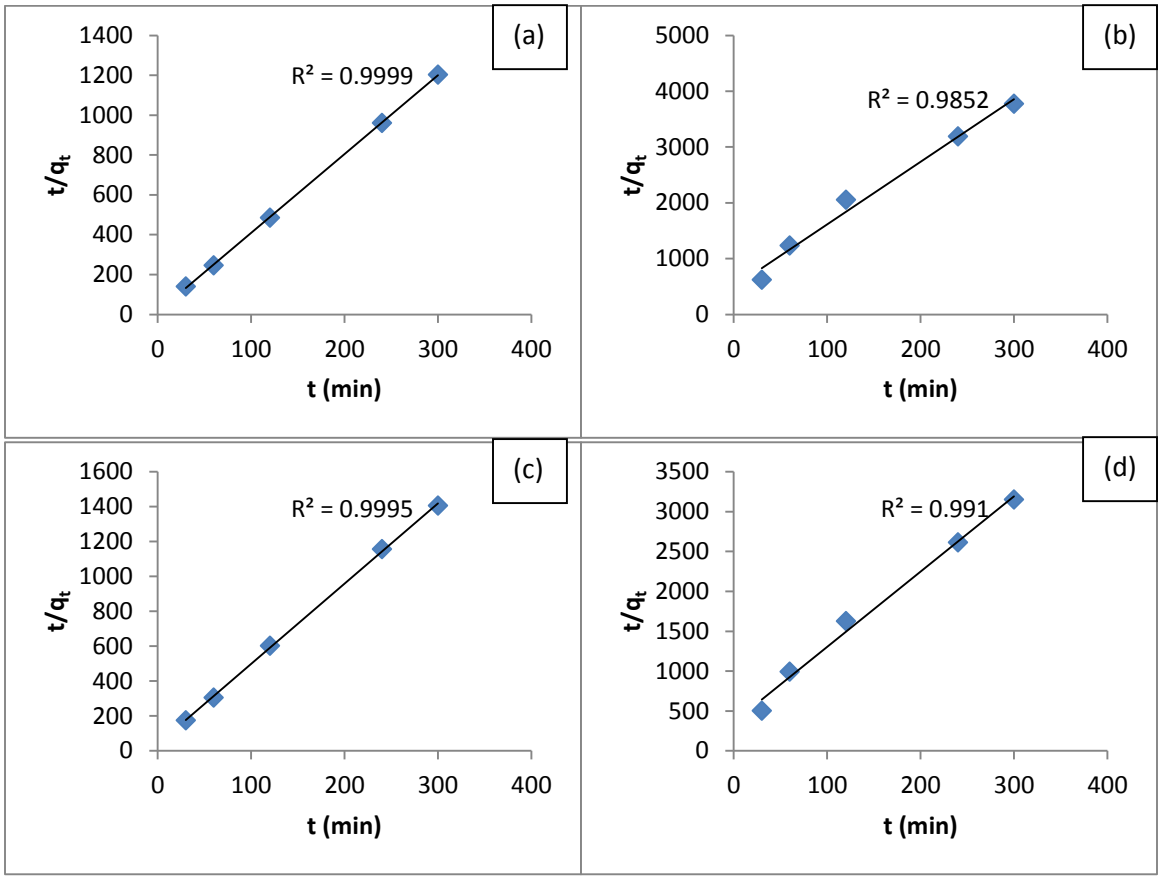

Figure 4.85 Pseudo second order kinetics of chromium on iron impregnated CNTs and AC (a) iron oxide – CNTs (b) iron oxide – AC (c) iron carbide – CNTs (d) iron carbide - AC

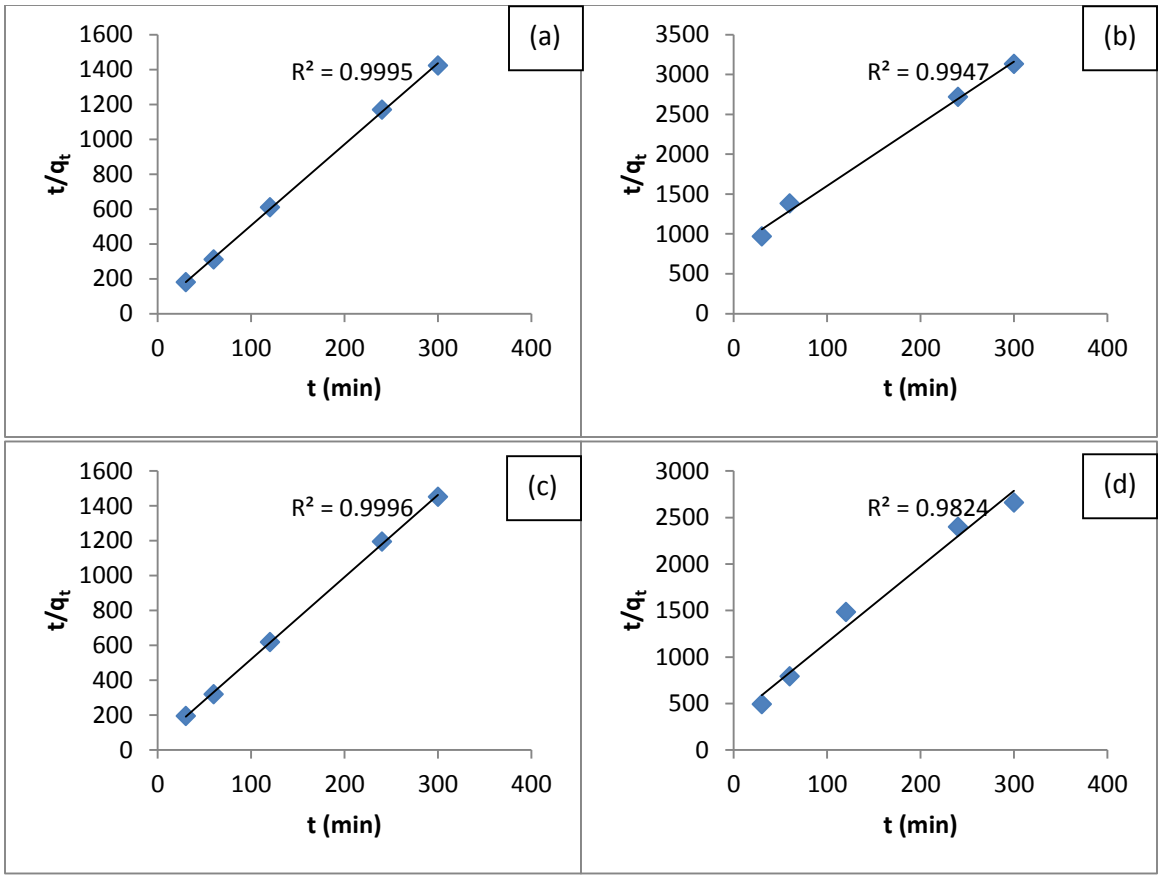

Figure 4.86 Pseudo second order kinetics of chromium on silver impregnated CNTs and AC (a) silver – CNTs (b) silver – AC (c) silver carbide – CNTs (d) silver carbide - AC

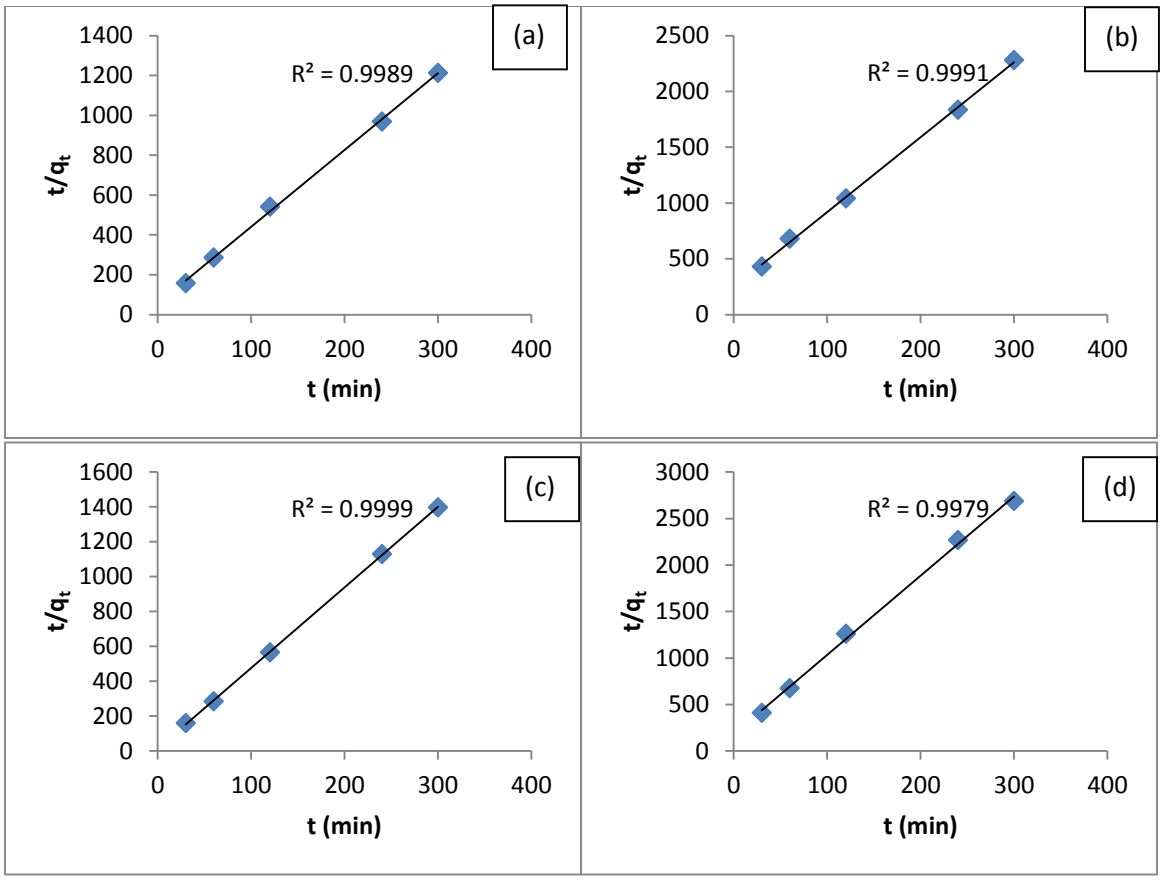

Figure 4.87 Pseudo second order kinetics of chromium on aluminium impregnated CNTs and AC (a) aluminium oxide – CNTs (b) aluminium oxide – AC (c) aluminium carbide – CNTs (d) aluminium carbide - AC

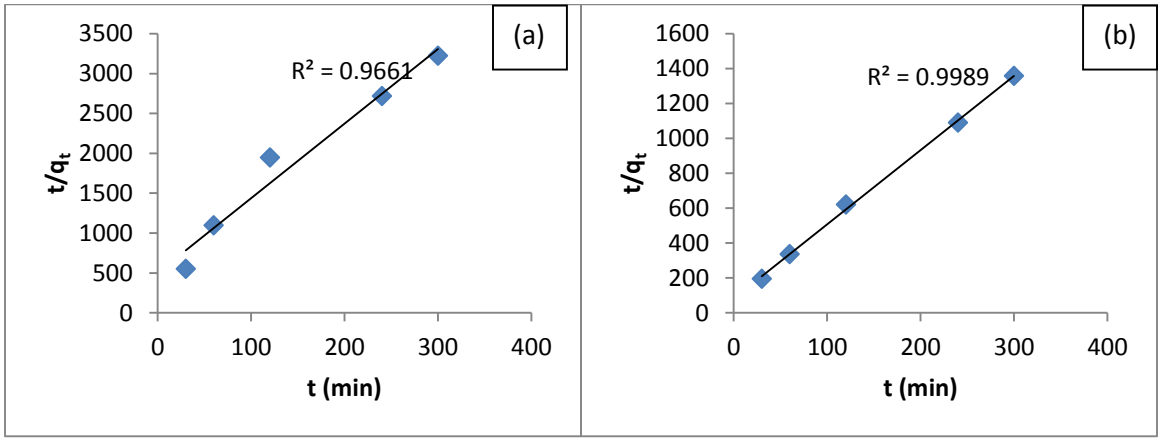

Figure 4.88 Pseudo second order kinetics of chromium on pure CNTs and AC (a) Pure AC (b) Pure CNTs

Table 4.6 Parameters of pseudo second order kinetic model for chromium

Adsorbent	q_e (mg/g)	k_2 (mg g^{-1} min^{-1})
Iron Oxide + CNT	0.253062	0.534162
Iron Oxide + AC	0.089138	0.127623
Iron Carbide + CNT	0.217463	0.268036
Iron Carbide + AC	0.105929	0.123373
Silver Oxide + CNT	0.215352	0.254458
Silver Oxide + AC	0.137142	0.024622
Silver Carbide + CNT	0.212183	0.225566
Silver Carbide + AC	0.122743	0.096725
Aluminium Oxide + CNT	0.259575	0.133789
Aluminium Oxide + AC	0.14884	0.091654
Aluminium Carbide + CNT	0.216389	0.763303
Aluminium Carbide + AC	0.117525	0.196578
Pure AC	0.106964	0.086564
Pure CNT	0.235297	0.109363

4.5.2. Kinetic Adsorption Modeling for Arsenic with CNTs and AC as Adsorbents

The adsorption kinetics was studied at a pH of 6. The parameters of modeling have been tabulated in Table4.7. The correlation coefficient of each plot is mentioned along each straight line plot.

Carboxylic group was attached onto the surface of CNTs and trivalent chromium was adsorbed onto it. The kinetics followed the pseudo second order model with high values of R^2. The value of adsorption capacity of modified CNTs at equilibrium (q_e) was found to be 0.5 in this case [35]. The maximum value of $q_e$in our work was recorded for silver carbide which is 0.88.

In a similar work mentioned above, the same type of CNTs were used for the removal of lead ions at a 1 ppm initial concentration. The results were quite similar in terms of the type of model and also the value of correlation coefficient for the adsorbents [56].

Following are the plots representing the fitting of experimental data with the pseudo second order model for adsorption kinetics. Each straight line represents its value of R^2 on the plot as well.

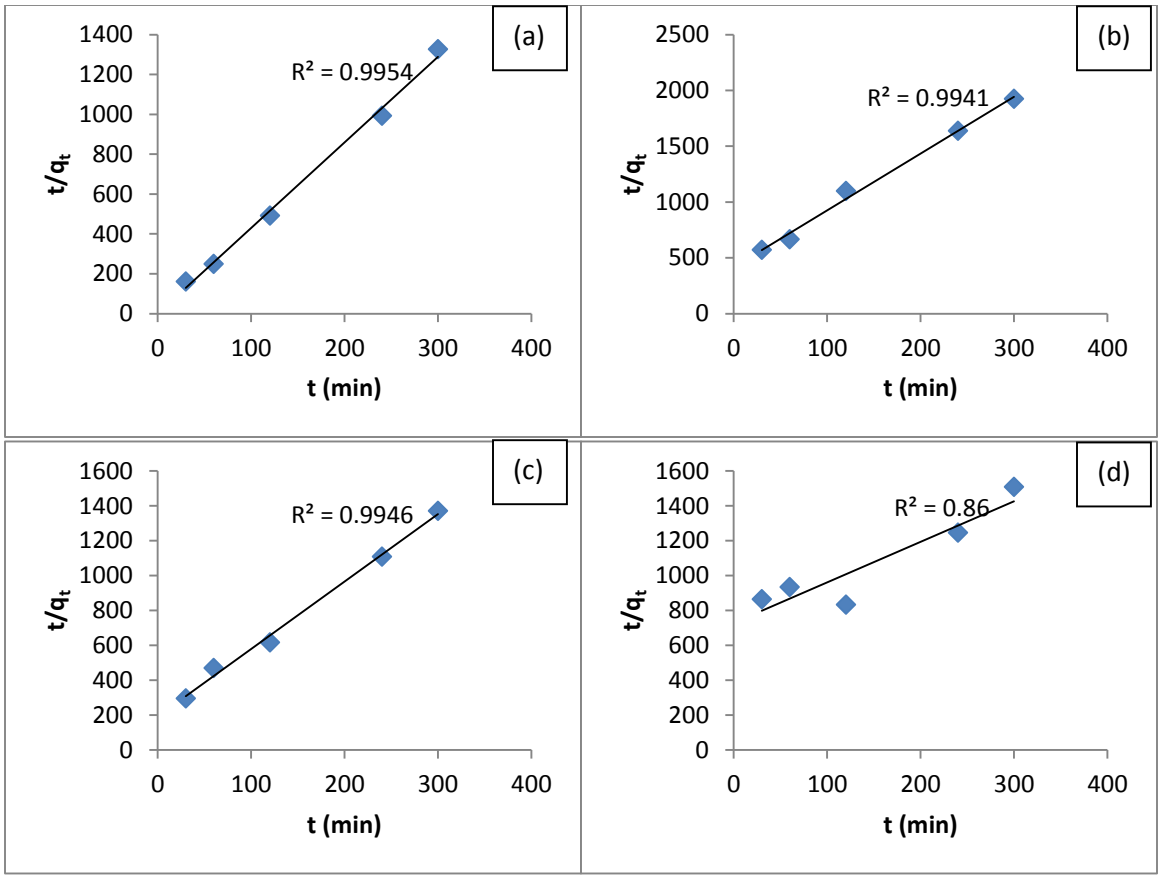

Figure 4.89 Pseudo second order kinetics of arsenic on iron impregnated CNTs and AC (a) iron oxide – CNTs (b) iron oxide – AC (c) iron carbide – CNTs (d) iron carbide – AC

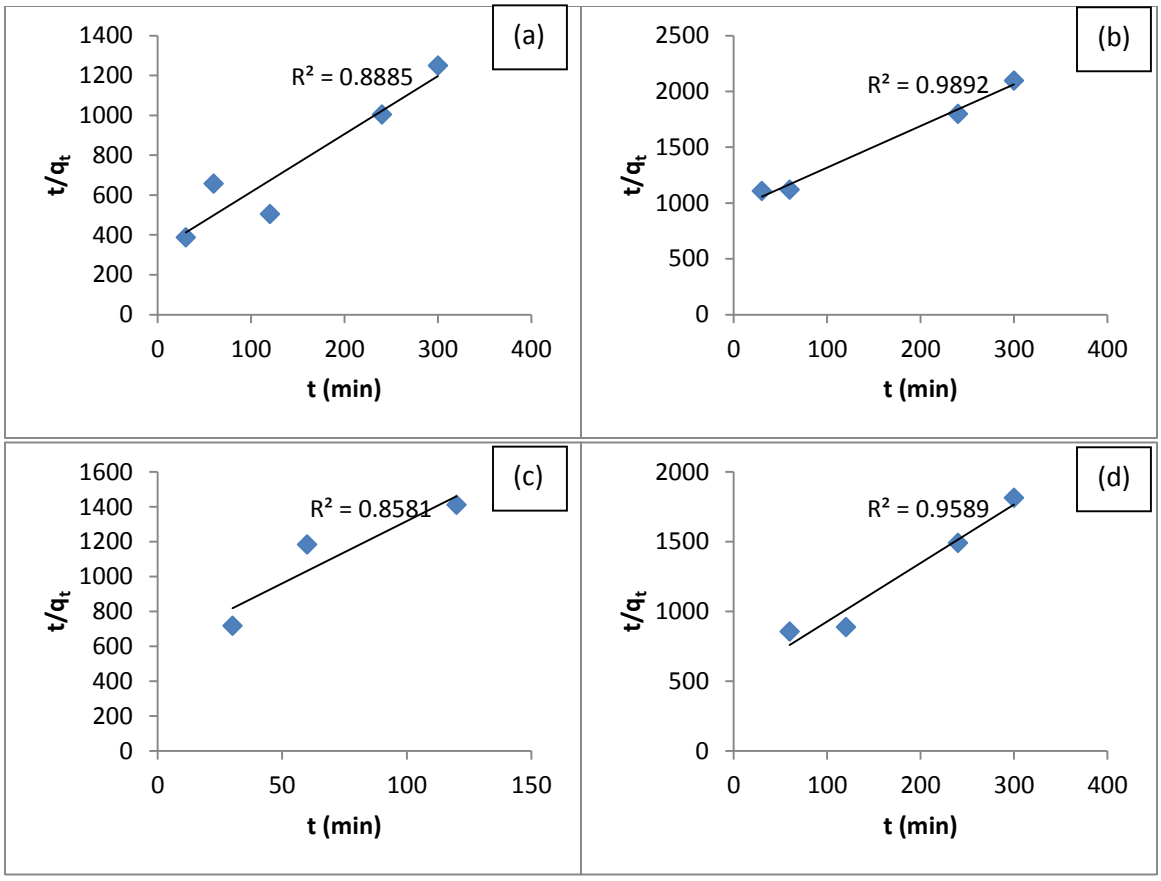

Figure 4.90 Pseudo second order kinetics of arsenic on silver impregnated CNTs and AC (a) silver – CNTs (b) silver – AC (c) silver carbide – CNTs (d) silver carbide – AC

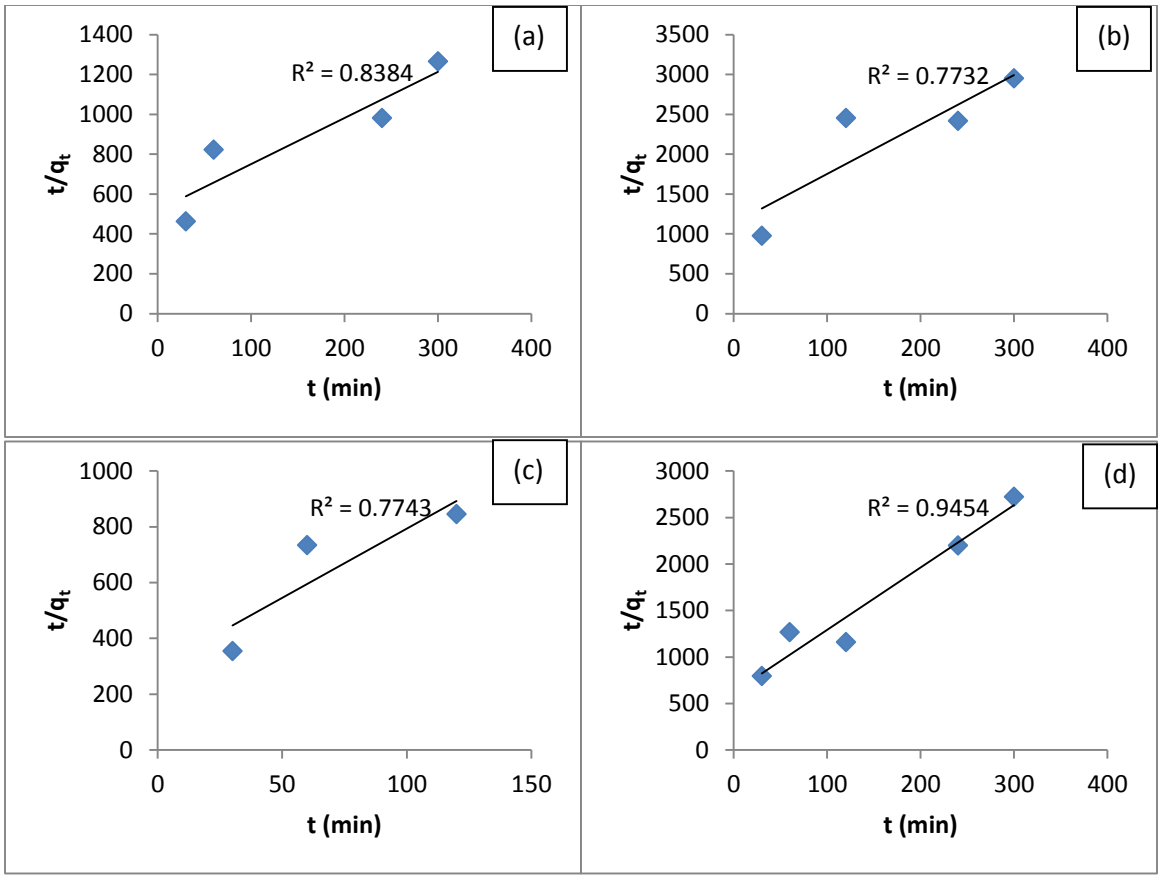

Figure 4.91 Pseudo second order kinetics of arsenic on aluminium impregnated CNTs and AC (a) aluminium oxide – CNTs (b) aluminium oxide – AC (c) aluminium carbide – CNTs (d) aluminium carbide – AC

Table 4.7 Parameters of pseudo second order kinetic model for arsenic

Adsorbent	q_e (mg/g)	k_2 (mg g^{-1} min^{-1})
Iron Oxide + CNT	0.245204	0.485168
Iron Oxide + AC	0.196676	0.03096
Iron Carbide + CNT	0.25853	0.038859
Iron Carbide + AC	0.429822	0.003716
Silver Oxide + CNT	0.34394	0.01302
Silver Oxide + AC	0.252019	0.009579
Silver Carbide + CNT	0.882217	0.000721
Silver Carbide + AC	0.424151	0.002929
Aluminium Oxide + CNT	0.411946	0.006407
Aluminium Oxide + AC	0.274647	0.003638
Aluminium Carbide + CNT	0.521238	0.002431
Aluminium Carbide + AC	0.149161	0.036059
Pure AC	0.268582	0.006909
Pure CNT	0.599147	0.001818

4.6. Comparative Analysis of Heavy Metals' Removal Using AC and CNTs

Here, we describe a comparison between the results obtained in this research work and similar work which has already been carried out with certain differences. The removal of

similar heavy metals using other adsorbents has been distinguished with the present work results.

Table 4.8 Comparative analysis of heavy metals' removal by different adsorbents with the present research

Type of Adsorbent	Type of Heavy Metal	pH	Adsorption capacity (q_m)	Reference
Acid modified CNTs	Cr (VI)	3	1.314	Ihsanullah (2015)
Acid modified AC	Cr (VI)	3	18.519	Ihsanullah (2015)
COOH functionalized CNTs	Cr (III)	7	0.3853	Muataz (2010)
COOH functionalized CNTs	Pb	7	6.6	Muataz (2010)
Ag – AC	As	8	3.24	Ljubinka V. Rajakovic (2014)
Cu – AC	As	8	14.61	Ljubinka V. Rajakovic (2014)

AC	Cr (III)	9	0.178	El – Sheikh (2008)
Aluminium carbide – CNTs	Cr (VI)	6	1.302	This study
Pure CNTs	Cr (VI)	6	0.737	This study
Silver carbide – CNTs	Cr (VI)	6	0.756	This study
Silver – AC	Cr (VI)	6	0.730	This study
Iron oxide – CNTs	Cr (VI)	6	0.438	This study
Aluminium oxide – CNTs	Cr (VI)	6	0.552	This study
Silver – AC	As	6	0.701	This study
Silver carbide – CNTs	As	6	0.708	This study
Aluminium carbide – AC	As	6	0.676	This study
Aluminium carbide – CNTs	As	6	0.661	This study

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The modification of CNTs and AC with metal oxides and metal carbides was worthy in the removal of heavy metals from aqueous solution. The adsorption experiments and their study reveals that the binding of these heavy metals depends upon various factors including the dosage of adsorbent, pH of solution, agitation speed and contact time. Moreover, Langmuir isotherm model depicted mono layer adsorption and the adsorption kinetics are followed by the pseudo second order model.

Characterizations of the synthesized materials show the required level of impregnation of metal compounds on each type of adsorbent. These adsorbents performed well on removal of the concerned heavy metals giving excellent results in most cases. The maximum removal of chromium was achieved by iron and aluminium oxide impregnated CNTs which was about 98% at a contact time of 2 hrs but as the time was increased, the removal reached almost 100% around 4 to 5 hrs of agitation time. In the case of arsenic, aluminium oxide impregnated CNTs were found to be the most useful adsorbent removing 99.9% of the contaminant. Iron oxide impregnated AC removed around 85% of chromium and 87% of arsenic after 5 hrs of contact time. 96% removal of arsenic and 84% removal of chromium was achieved with silver impregnated CNTs. Silver carbide impregnated CNTs were able to remove 86% of chromium and 88% of arsenic in the same time period. Similarly, aluminium carbide impregnated CNTs were efficient to about 83% removal of arsenic and 86% removal of chromium. All these results depict extreme potential in metal oxide and metal carbide impregnated CNTs and AC for the removal of heavy metals from water.

Langmuir isotherm model was found to give the best fit with the experimental data of heavy metal removal giving excellent values of the correlation coefficient. Iron oxide impregnated CNTs gave the maximum value of R^2 which was 0.9966 for chromium and 0.9893 for arsenic. On the other hand, silver impregnated AC gave a value of 0.9949 for arsenic removal (Fruendlich isotherm). The adsorption kinetics was found to follow the pseudo second order kinetics model. R^2 value for iron oxide – CNTs was found to be 0.9999 for the removal of chromium and 0.9954 for arsenic removal, which is the highest in both cases. Silver carbide – CNTs gave the highest value for adsorption capacity at equilibrium for arsenic i.e. 0.8822 and iron oxide – CNTs gave the highest for chromium which was 0.25.

Thus, it can be inferred that CNTs and AC modified with metal nanoparticles are potential adsorbents for heavy metals like chromium and arsenic. Although, CNTs are categorized as expensive materials yet they have all capabilities of efficiently removing heavy metals from water. In contrast, AC is a less expensive material and it has shown exceptional results in this study with various impregnations on its surface. However, this is not the end. There are plenty of avenues which can be exploited in this regard. Some recommendations which can be put forth considering this study are listed below:

1- Similar adsorbents should be tried with multi element (heavy metal) aqueous solutions to observe any possible effects that can take place during mutual adsorption of metal ions.

2- This study should be taken a step forward by using real samples of waste water containing heavy metals and perform a check on the removal of these contaminants using the same adsorbents.
3- The desorption of contaminants from the adsorbents should be studied in order to regenerate the adsorbents and use them time and again to rectify the constraint of high costs as in the case of CNTs.
4- CNTs and graphene are similar materials with different orientations which require more similar studies using graphene as the adsorbent and a comparison of the results with those of CNTs and AC.
5- More types of metal should be impregnated onto adsorbent surfaces and checked for adsorption of heavy metals.
6- Apart from heavy metals, many other contaminants are present in water and wastewater which should be addressed using the same modification of carbon adsorbents.
7- The leaching of adsorbent material should be studied in order to minimize the effects of pollution of these materials onto human health.

Without a doubt the results of this project are satisfactory with regards to the objectives described and the extent to which they are achieved. The need of the hour is to take this research to a much higher level and try to make it beneficial for the society which is possible through applications in industry. Being at a basic scale, hopefully, this research will benefit science and the society as a whole.

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